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STAIN REMOVAL

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The portion of the term of the patent subsequent to Jan. 25, 1989, has been disclaimed
Int. Cl. C11d 7/54
U.S. Cl. 252—99 11 Claims

ABSTRACT OF THE DISCLOSURE

Composition for removing stains from fabrics, including an enzyme, a per-compound, and an activator for the perborate.

This application is a division of application Ser. No. 726,571, filed May 3, 1968, now U.S. Pat. No. 3,637,339, issued Jan. 25, 1972, which patent was a continuation-in-part of my copending application Ser. No. 711,203, filed Mar. 7, 1968 and now abandoned.

This invention relates to stain removal and detergency.

The use of proteolytic enzymes as assistants in the laundering of clothes with detergent compositions has long been known in the art. While combinations containing both enzymes and sodium perborate, a well known bleaching agent used in detergent products, have been suggested, the art has taught that the presence of the perborate has an inhibitory effect on the enzyme action, which inhibitory action passes away, in part, after some time (e.g. on soaking overnight in the presence of the detergent composition). The use of bleaches of greater activity than sodium perborate, such as "chlorine bleaches" (supplied for instance by the use of a chloroisocyanurate material which yields hypochlorous ions in the wash water) has a marked inhibiting effect on the stain-removing activity of detergen porducts containing enzymes.

In accordance with one aspect of this inveniton there is provided a novel and highly effective composition for use in the washing of clothes comprising a mixture of a proteolytic enzyme, sodium perborate and an activator for the perborate. Surprisingly, in the presence of the activator one can obtain, in a short washing cycle, and at a moderate washing temperature, not only improved bleaching of those stains (e.g. coffee and tea stains) as are usually affected by bleaching compositions but also the removal of proteinaceous stains to an extent equal to or better than is obtained when the perborate and activator are omitted.

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 4–12, such as usually prevails in detergent cleaning procedure. 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, collaginase, keratinase, carboxylase, amino peptidase, elastase, subtilisia and aspergillopeptidase A and B. They are available also under names such as Alcalase (Novo Industri, Copenhagen,

Denmark), Monzyme (Monsanto Chemical Co.), Maxatase (Royal Netherlands Fermentation, Delft, Netherlands), Protease AP (Sandoz-Ferment, Basel, Switzerland), Protease B–400 (Sandoz-Ferment), Protease ATP 40 (Sandoz-Ferment), Pancreatin NF (Pfizer), Pancreatin 6xNF (Armour), Fungal Protease (Miles), DSE Numbers 4–9 (Rohm and Haas), Exzyme DPX (Premier Malt), Protease L–252 Digester (Premier Malt), Protease L–253 Digester (Premier Malt), Protease L–423 (Premier Malt), Protease L–516 (Premier Malt), Protease L–517 (Premier Malt), Texzyme PX–1 (Premier Malt), Protease P-G (Pfizer), Compound 37B (Miles), Serizyme (Wallerstein), Papain 100 (Wallerstein), Opimo Papain (Penick), Ficin (Miles), Bromelain (Miles), HT Proteolytic Concentrate (Miles), Protease ATP 40 (Rapidase), Protease ATP 120 (Rapidase), Rhozyme P–11 (Rohm and Haas) and Rhozyme PF (Rohm and Haas).

Proteolytic enzymes such as Alcalase, Maxatase, Protease AP, Protease ATP 40, Protease ATP 120, Protease L–252 and Protease L–423 are derived from strains of spore foaming Bacillus, suchc as *Bacillus subtillis.*

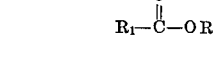
Different proteolytic enzymes have different degrees of effectiveness in aiding in the removal of stains from textiles and linen. Particularly preferred as stain removing enzymes are Alcalase, Maxatase, Protease AP, Protease ATP 40, and Rapidase.

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

The perborate activators are a well known class of materials, described for example in a series of articles by Gilbert in Detergent Age, June 1967 pages 18–20, July 1967 pages 30–33, and August 1967 pages 26, 27 and 67. The perborate activators of greatest importance in the practice of this invention are compounds which are percarboxylic acid precuresors. As explained by Gilbert, such compounds include esters and anhydro and acyl amides. Examples of suitable activators are given by Gilbert who also describes a test for suitability. Among the activators which may be used are the following:

N-acetyl phthalimide
N-acetyl succinimide
trisacetyl cyanurate
N-benzoyl succinimide
Phenyl acetate
Acetylsalicylic acid
N-p-anisoyl succinimide
N-alpha-naphthoyl succinimide
N-beta-napthoyl succinimide
N-benzoyl glutarimide
N-p-chlorobenzoyl succinimide
N-benzoyl succinimide
N-p-chlorobenzoyl-5,5-dimethyl hydantoin
N-o-chlorobenzoyl succinimide
N-p-chlorobenzoyl phthalimide . . . etc.

Further examples of suitable activator compounds of the imide type, both cyclic and aliphatic, have the following structural formula:

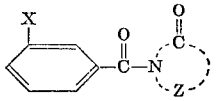


wherein R represents alkyl and preferably lower alkyl of 1 to 4 carbon atoms or aryl such as phenyl and R_1 represents an N-bonded imide radical. Thus, included within the foregoing structural formula are the following:

N-methoxycarbonyl saccharide
N-methoxycarbonyl phthalimide
N-ethoxycarbonyl phthalimide
N-methoxycarbonyl-5,5-dimethyl hydantoin

N-methoxycarbonyl succinimide
N-phenoxycarbonyl succinimide
N,N-di-(methoxycarbonyl) acetamide
N-methoxycarbonyl glutarimide
1,3-di-(N-methoxycarbonyl)-hydantoin
1,3-di-(N-methoxycarbonyl)-5,5-dimethyl hydantoin

Other suitable activator compounds are represented according to the following structural formula:

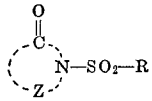


wherein X represents halogen e.g. chloro and Z represents the atoms necessary to complete a heterocyclic nucleus selected from the group consisting of hydantoin and succinimide.

Specific representatives of compounds of this type include, without necessary limitation, the following:

N-m-chlorobenzoyl-5,5-dimethyl hydantoin
N-m-chlorobenzoylsuccinimide . . . etc.

Another group of activator compounds comprises N-sulfonated cyclic imides including those of the following structural formula:



wherein R represents lower alkyl of from 1 to 4 carbon atoms and aryl and Z represents the atoms necessary to complete a heterocyclic ring selected from the group consisting of succinimide and phthalimide. Specific examples of compounds of this type include, without necessary limitation, the following:

N-benzenesulfonyl phthalimide
N-benzenesulfonyl succinimide
N-methanesulfonyl phthalimide
N-methanesulfonyl succinimide

A further class of activator compounds comprises alkyl and aryl chloroformate derivatives, including for example:

methylchloroformate
ethylchloroformate
phenylchloroformate

The proportions of per-compound, activator, and enzyme will be influenced by the physical and chemical properties of these ingredients, the time and temperature of the bleaching or laundering operation, and the degree of bleaching desired.

A preferred range of proportions of the perborate is one which provides a concentration of per compound in the wash water equivalent to about 1 to 40 p.p.m. more preferably about 4 to 25 p.p.m., e.g. 8 to 20 p.p.m., of available oxygen; about 20 p.p.m. has thus far given best results. In sodium perborate tetrahydrate ($NaBO_3 \cdot 4H_2O$) the available oxygen content (or peroxy oxygen content) is about 10%; i.e. one atom of available oxygen per molecule of the perborate. The proportions of perborate for use in the detergent formulation can therefore readily be calculated if one knows how much of the total formulation is to be added to the wash water. Commercial detergent formulations are often designed for use in proportions in the range of about 0.1–0.2% in the wash water (e.g. at 0.15% concentration), a preferred detergent formulation containing sodium perborate tetrahydrate designed for use at the 0.15% concentration in the wash water will therefore contain approximately 5 to 15% of that compound, corresponding roughly to the 8 to 20 p.p.m. of available oxygen.

Since individual activators vary in structure and molecular weight as well as performance, it is convenient to relate the quantity of activator to be employed to the desired available oxygen present in the particular per-compound being used. For reactive aromatic mono-acyl compounds such as metachlorobenzoyldimethylhydantoin and meta-chlorobenzoylsuccinimide, strong bleaching is obtained when approximately equimolecular quantities of activator and peroxygen are present. Bleaching is enhanced with increase in the concentration of activator and maintenance of about a 1:1 mol ratio of activator and the peroxygen present in the per-compound. By increase of the mol ratio of available oxygen to activator, milder bleaching is obtained particularly when the ratio is greater than 2:1. For reactive aliphatic poly-acylated compounds such as tetra-acetylethylenediamine, tetra - acetylhydrazine, triacetyl cyanurate, the mole ratio of available oxygen to activator is preferably 2:1, although higher (e.g. 6:1) or lower (e.g. about 1:1 or less) mol ratios may be employed.

The enzyme concentration can be varied widely. Typically the enzyme is present in amount in the range of about 0.001%–4% by weight of the total detergent formulation, preferably in the range of about 0.05–1% and most preferably in the range of about 0.1 to 0.5%. The optimum proportion of enzyme to be used in a detergent composition containing per-compound and activator will of course depend upon the effective enzyme content of the enzyme preparation. As with per-compound 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 per-compound and activator. For the enzyme sold as Alcalase (having an activity of about 1.5 Anson units per gram) a preferred range of proportions is one which gives about 1 to 40 p.p.m., more preferably about 2–8 p.p.m., of the Alcalase in the wash water. This 2–8 p.p.m. concentration corresponds to about 0.003–0.012 Anson units per liter of wash water or, in a detergent formulation designed for use at a concentration of 1.5 gram per liter of wash water, about 0.002–0.008 Anson units per gram of detergent formulation.

The enzyme, perborate and activator 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.

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 non-ionic 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, cocoanut 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 dimonyl naphthalene sulfo-

nate; sulfated aliphatic alcohols such as sodium lauryl and hexadecyl sulfate, 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 hydroxylethyl 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, 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; 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 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-aminoethyl 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, methosulfate, etc. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethylcetyl ammonium bromide, methylethyl-dilauryl ammonium chloride, dimethyl-propylmyristyl 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), albali 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 presentin powdered form admixed into the detergent formulation.

In addition to the materials described above, the detergent composition of the inveniton 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, 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%, 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 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 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-naphtho-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-2yl-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 activator, enzyme and perborate may be added in powdered form to the detergent composition and mixed therewith, as a 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. For instance, the perborate or the activator or the enzyme or each of them may be encapsulated or agglomerated by means of a coating of a protective material such as polyvinyl alcohol, a long chain fatty acid (e.g. lauric or stearic) or an amide thereof, a paraffin or a water-soluble or water-dispersible polyethylene glycol (e.g. a solid "Carbowax"). It is also 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 80–100° F., or in warm or hot water, e.g. at 110°, 120°, 140°, or 160° F., 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, e.g. for soaking several hours or overnight.

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

EXAMPLE 1

(A) A detergent composition contains the following ingredients: 10% nonionic detergent consisting of a primary alkanol of an average of 14 to 15 carbon atoms ethoxylated with an average of 11 mols of ethylene oxide per mol of alkanol (Shell "Neodol 45–11"); 30% anhydrous pentasodium tripolyphosphate (designated "TPP" below); 5% trisodium nitrilotriacetate monohydrate (designated "NTA" below); 0.5% sodium carboxymethyl cellulose (designated "CMC" below); 0.8% of the commercial proteolytic enzyme preparation known as "Alcalase"; 16% of sodium perborate ($NaBO_3 \cdot 4H_2O$); 24% of meta-chlorobenzoyldimethylhydantoin (an activator for the perborate); the balance sodium sulfate. In this composition the mol ratio of perborate to activator is about 1:1 (specifically it is 1.1:1).

The composition is used for the washing of standard cocoa-stained fabrics and standard coffee/tea-stained fabrics at 120° F. for a period of 10 minutes, using 1 gram of the composition per liter of water in a Terg-O-Tometer. The effectiveness of the composition is determined by reflectance readings ("R_d") on the fabrics before and after washing, using a Gardner Color Difference Meter for the measurement. The difference in reflectance before and after the washing is reported as "ΔR_d". Cocoa is a proteinaceous substance and cocoa-stained fabric is a commonly used material for testing the effectiveness of detergents for removing protein stains.

For comparison the same washing tests are made on otherwise identical compositions, (B) containing no enzyme, perborate or activator; (C) containing enzyme, but no perborate or activator; and (D) containing the enzyme plus a commercial bleach yielding hypochlorous ion (specifically a mixture of ⅘ potassium dichloroisocyanurate ("KDCC") and ⅕ trichloroisocyanuric acid ("TCCA"). The results are tabulated below:

	A	B	C	D
Composition, percent:				
Detergent	10	10	10	10
TPP	30	30	30	30
NTA	5	5	5	5
CMC	0.5	0.5	0.5	0.5
"Alcalase"	0.8	----	0.8	0.8
Perborate	16	----	----	----
Activator	24.8	----	----	----
KDCC–TCCA	----	----	----	18.1
Na_2SO_4	Q.S.	Q.S.	Q.S.	Q.S.
ΔR_d:				
For cocoa-stained fabric	+13.4	+7.6	+11.0	+4.8
For coffee/tea-stained fabric	+8.0	−0.1	+0.4	+8.2

The foregoing results show that on addition of the perborate plus activator to the enzyme-containing composition, there is a marked improvement in detergency for the protein stain even in the short washing period of 10 minutes, at a moderate washing temperature. In contrast when another strong oxidizing agent (the chlorine bleach, KDCC–TCCA) is used with the enzyme the protein stain removal effectiveness drops to below even the level obtained for the enzyme-free composition. The activator-perborate-enzyme composition is also highly effective for removal of coffee/tea stain.

EXAMPLE 2

In this Example an enzyme, sodium perborate and activator are dry-blended with a spray-dried detergent formulation having the following composition: sodium linear tridecylbenzenesulfonate 12.6% (active ingredient); sodium tallow alcohol sulfate 11.6% (active ingredient); TPP 35.8%; sodium silicate (of 1:2.35 $Na_2O:SiO_2$ ratio) 6.3%; CMC 0.5%; polyvinyl alcohol 0.2%; water (including water of hydration) 8.9%; Na_2SO_4, balance. Two blends are prepared, of the following compositions, in parts by weight:

Composition	A	B
Spray dried detergent formulation	1.5	1.5
Alcalase	0.008	----
Monzyme	----	0.002
Sodium perborate	0.16	0.16
Activator of Example 1	0.248	0.248

EXAMPLE 3

Examples 2 A and B are repeated except that the spray-dried detergent has a different composition and is made in the following manner: In a crutcher there are mixed in the order given 139 parts of water, 213 parts of an aqueous slurry containing about 44% sodium linear tridecylbenzenesulfonate, 109.3 parts of anhydrous sodium sulfate, 4.4 parts of borax, 0.13 part of phenolic antioxidant (Iphol 033), 71.4 parts of aqueous sodium silicate of 43.5% concentration (in which the $Na_2O:SiO_2$ mol ratio is 1:2.35), and 157 parts of anhydrous pentasodium tripolyphosphate. The aqueous mixture is spray-dried to give a granular composition of the foregoing ingredients having a total moisture content of about 8½% (including water of hydration).

EXAMPLE 4

In this Example there are used compositions as described in Example 1A, except that the activator is (A) 11.9% of tetraacetylethylenediamine or (b) 10.4% tetraacetylhydrazine, or (C) 13.3% triacetylcyanurate. For comparison there are also used compositions (D) containing no activator and (E) containing no activator or perborate.

The compositions are used for the soaking of standard cocoa-stained and standard coffee/tea-stained fabrics, using 1 gram of the composition per liter of water. The water is initially at 120° F. and cools to room temperature (about 76° F.) during the soaking period, which is continued for 18 hours. The test fabrics are removed and dried and the ΔR_d values are obtained.

The results are tabulated below:

	A	B	C	D	E
Composition:					
Detergent, percent	10	10	10	10	10
TPP, percent	30	30	30	30	30
NTA, percent	5	5	5	5	5
CMC, percent	0.5	0.5	0.5	0.5	0.5
Alcalase, percent	0.8	0.8	0.8	0.8	0.8
Perborate, percent	16	16	16	16	----
Perborate:activators, mol ratio	2:1	2:1	2:1	(1)	----
Na_2SO_4	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
Δ Rd:					
For cocoa-stained fabric	+10.1	+10.9	+13.2	+5.2	+10.2
For coffee/tea-stained fabric	+5.9	+5.5	+6.5	+1.7	+2.7

[1] No activator.

These results indicate that the addition of the perborate to an enzyme-containing composition in a soaking test gives poorer results, both for the protein-containing stain and the coffee/tea stain, than when perborate is absent.

The addition of the activator improves the stain removal not only for the coffee/tea stain but also for the protein stain.

A composition prepared as in Example 4A is storage-tested by subjecting it for 3 days to a temperature of 120° F. in a sealed container. During this period there is little, if any, undesirable odor developed. Soaking tests with standard cocoa-stained and coffee/tea-stained fabrics give substantially identical results for the composition before the 3 day aging at 120° F. and after such aging.

EXAMPLE 5

Three separate compositions are prepared as in Example 1A, using tetra-acetylethylenediamine (i.e. N,N,N',N'-tetraacetylethylenediamine) as the activator in each case, with the following other changes:

A. The amount of activator is changed to 11.9% and the amount of TPP is changed to 54.5%.

B. The amount of activator is changed to 8.9% and the amount of perborate is changed to 12.0%.

C. The amount of activator is changed to 7.4% and the amount of perborate is changed to 10.0%.

EXAMPLE 6

81.8 parts of a spray-dired built detergent formulation are mixed with 0.8 part of Alcalase, 7.4 parts of tetra-acetyl ethylenediamine and 10 parts of sodium perborate. The spray-dried formulation contains 10.5% sodium linear tridecylbenzenesulfonate, 51% pentasodium tripolyphosphate, 6% sodium silicate ($Na_2O:SiO_2$ mol ratio 1:2.35), 8.5% sodium chloride, 13% sodium sulfate, 10% moisture (including water of hydration) and about 1% fluorescent brighteners.

The resulting composition is tested, using the washing tests described in Example 1. The results, in terms of ΔR_d, for the cocoa-stained and coffee-tea-stained fabrics are found to be substantially better than those for the same tests using the same composition except that no perborate or activator is present (these being replaced by an equal weight of sodium sulfate); the latter results are in turn substantially better (in terms of removal of cocoa stain) than when the same composition is used without any enzyme, perborate or activator (these being replaced by an equal weight of sodium sulfate).

The composition is also given a soaking test, as described in Example 4. The results, in terms of ΔR_d, for the cocoa-stained and coffee/tea-stained fabrics are to be substantially better than those for the same tests using the same composition except that no perborate or activator is present (these being replaced by an equal weight of sodium sulfate); the latter results are in turn substantially better than when the same composition is used without any enzyme, perborate or activator (these being replaced by an equal weight of sodium sulfate). In the same type of soaking test, made after the compositions have been aged for 3 days at 120° F. in sealed containers, a similar superiority for the enzyme-containing composition with perborate plus activator is observed.

EXAMPLE 7

Example 1A is repeated, except that the composition contains 100 parts of the detergent of Example 1, 300 parts of the TPP, 50 parts of the NTA, 5 parts of the CMC, 240 parts of the sodium perborate and 371 parts of m-chlorobenzoylsuccinimide as the activator.

EXAMPLE 8

Example 1A is repeated using, in place of the activator and perborate, 25% of solid m-chloroperbenzoic acid.

EXAMPLE 9

Example 4 is repeated, except that the amount of the perborate is 8% and the activator is m-chlorobenzoyldimethylhydantoin, present in amount of 13.9% (a 1:1 perborate; activator mol-ratio) ΔR_d values of +15.4 (for cocoa-stained fabric) and +6.9 (for coffee/tea-stained fabric) are obtained.

The "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 the enzyme. The commercial enzyme is a raw extract of *Bacillus subtillis* culture and contains about 6% of pure crystallized proteolytic material.

The "Monzyme" used in Example 2 and 3 is a mixture of neutral and alkaline proteases (the neutral protease being present in largest amount) containing amylase also; its supplier, Monsanto Chemical Co., states that its proteolytic activity is about one million units per gram.

In each of the above Examples sodium perborate tetrahydrate is used; other forms of sodium perborate, such as the monohydrate, may be substituted in each case.

The pH of the wash liquor in the foregoing Examples, measured in each case after completion of the washing test, is usually within the range of about 8 to about 9.

While the invention finds its greatest utility when sodium perborate is employed, other perborates (such as $LiBO_3 \cdot 2H_2O$, $LiBO_3 \cdot H_2O$, $KBO_3 \cdot \frac{1}{2}H_2O$ or barium or calcium perborates) may be used in place of all or part of the sodium perborate. Also other agents which convert the normally stable activator into a percarboxylic acid(or salt thereof) in the wash water may be used in place of the perborate, e.g. percarbonates or perphosphates.

It is within the broader scope of the invention to use a percarboxylic (i.e. peroxycarboxylic) acid, particularly a solid percarboxylic acid, instead of the combination of perborate and activator. Among such percarboxylic acids are the peroxybenzoic acids, particularly those having chloro or nitro substituents (e.g. m-chloroperoxybenzoic acid, as illustrated in Example 6 above, or 2,4-dichloroperoxybenzoic acid). These acids may be protected against deterioration on storage by pelletizing them, preferably with a coating or agglomerating agent such as a low-melting paraffin wax.

As indicated above, the compositions of the invention containing proteolytic enzymes have given outstanding results. Also, as shown in Examples 2 and 3, a proteolytic enzyme mixed with an amylase ("Monzyme") may also be employed. It is within the broader scope of the invention to use other enzymes in place of, or together with, the proteolytic enzymes. Thus, such stain-attacking enzymes as the amylases (such as the microbial amylases) or other carbohydrases (e.g. maltase, saccharase, pectinase, lysozyme, or glycosidases) or the lipsaes such as microbial lipases, pancreatic lipase, plant lipases or gastric lipase may be used. Specifically, in the composition of Example 1A, the "Alcalase" may be replaced entirely (or partly) weight-for-weight by either (a) Novo bacterial amylase concentrate having a strength of 397,000 Novo amylase units per gram or (b) Pfizer's Lipase P, a pancreatic lipase having a strength of 250 lipase units per gram.

Especially for use in areas where the water has a relatively high heavy metal content, it may often be desirable to have present a compound acting as a stabilizer against an undesirable type of decomposition of the perborate. Among such compounds are the sodium salts of diethylenetriamine pentaacetic acid, ethylene diamine tetraacetic acid, hydroxyethylethylenediamine triacetic acid or nitrilotriacetic acid. Magnesium silicate may also be present to aid in the stabilizing effect. Minor amounts of these agents, e.g. 5%, 1% or less are effective.

It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of the invention.

What is claimed is:

1. A composition consisting essentially of effective amounts of an inorganic peroxygen compound, an activa-

tor for the peroxygen compound and about 0.001% to 4% of a proteolytic enzyme, said activator having a carboxylic acyl group, said peroxygen compound being one which reacts with said activator to form the corresponding percarboxylic acid on addition of said composition to wash water, said activator being present in amount effective to so convert said peroxygen compound and thereby increase the bleaching effect of said peroxygen compound on coffee/tea stains, said composition being adapted to be added to aqueous wash water in an amount sufficient to provide about 1 to 40 p.p.m. of available oxygen to the wash water.

2. A composition as in Claim 1 in which the inorganic peroxygen compound is sodium perborate and the activator is selected from the group consisting of a carboxylic ester activator, a carboxylic anhydride activator and a carboxylic acyl amide activator.

3. A composition as in Claim 2 in which the activator is a benzoyl compound.

4. A composition as in Claim 3 in which the activator is meta-chlorobenzoyl dimethylhydantoin.

5. A composition as in Claim 2 in which the activator is a polyacyl amide.

6. A composition as in Claim 5 in which the activator is a polyacyl amide having a pair of carboxylic acyl groups on a single nitrogen atom.

7. A composition as in Claim 6 in which the acyl groups are acetyl.

8. A composition as in Claim 7 in which the activator is N,N,N',N'-tetra-acetylethylenediamine.

9. A composition as in Claim 1 containing an organic surface-active detergent.

10. A composition as in Claim 1 containing a builder salt.

11. A composition as in Claim 1 containing pentasodium tripolyphosphate and sodium nitrilotriacetate.

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