

PATENT SPECIFICATION

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(54) STAIN REMOVAL AND DETERGENCY

(71) We, COLGATE - PALMOLIVE COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to stain removal and detergency.

In accordance with one aspect of this invention a composition for use in washing stains from fabrics comprises an enzyme, e.g. a proteolytic enzyme or protease, and a material which supplies a percarboxylic acid or salt thereof when the composition is added to the wash water.

The material may be, for example, a per-compound, e.g. a perborate such as sodium perborate, and an activator therefor.

Surprisingly, with such a composition 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) which are usually attacked by leaching compositions but also the removal of proteinaceous stains to an extent equal to or better than is obtained when the said material is omitted.

The proteolytic enzymes which are preferably employed in performing the invention are active upon proteinaceous matter and catalyze digestion or degradation of such matter when present in linen or other fabric stains, for example, by a hydrolysis re-action. The enzymes are effective at a pH range of 4 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 80°C and even higher. They are also effective at ambient temperature and lower, e.g. down to 10°C. Particular examples of proteolytic enzymes which may be used are pepsin, trypsin, chymotrypsin, papain, bromelain, collagenase, keratinase, carboxylase, amino, peptidase, elastase, subtilisin and aspergillopeptidase A and B. Preferred enzymes manufactured and cultivated from *Bacillus subtilis*.

Metalloproteases which contain divalentions such as calcium, magnesium or zinc bound to their protein chains are also useful.

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 enzyme material may be 0.149 mm or smaller. On the other hand spray dried granules are usually of very much larger particle size, the major portion of the granules being at least 0.2 mm in diameter, e.g. from 0.3 to as large as 2 mm.

The enzyme preparations are generally diluted with salts such as calcium sulphate and other inert materials. Chemically they are usually stable in the pH range 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 higher temperatures to more than 1 day at lower temperatures in the range. Different proteolytic enzymes have different degrees of effectiveness in aiding in the removal of stains from linen and other textiles.

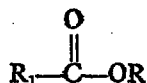
The per-compound activators are a well known class of materials, described for example in a series of articles by Gilbert in

"Detergent Age", June 1967, pages 18—20, July 1967, pages 30—33 and August 1967, pages 26, 27, and 67.

The activators are per-carboxylic acid precursors. As explained by Gilbert, such compounds include carboxylic esters and anhydrides and carboxylic 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-naphthoyl 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.

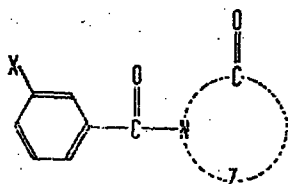
Further examples of suitable activator compounds of the imide type, both cyclic and aliphatic, have the following structural formula:



wherein R represents alkyl, preferably lower alkyl of 1 to 4 carbon atoms, or aryl such as phenyl, and R₁ 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:

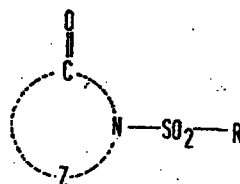


wherein X represents halogen, e.g. chloro, and Z represents the atoms necessary to complete a hydantoin or succinimide ring.

Specific representatives of compounds of this type include the following:

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

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



wherein R represents lower alkyl of from 1 to 4 carbon atoms or aryl, and Z represents the atoms necessary to complete a succinimide or phthalimide ring. Specific examples of compounds of this type include the following:

N-benzenesulphonyl phthalimide
N-benzenesulphonyl succinimide
N-methanesulphonyl phthalimide
N-methanesulphonyl 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 per-compound is one which provides a concentration of per-compound in the wash water equivalent to 1 to 40 ppm, more preferably 4 to 25 ppm, e.g. 8 to 20 ppm, of available oxygen; 20 ppm has so far given best results. For example, in sodium perborate tetrahydrate (NaBO₃ · 4H₂O) 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 0.1 to 0.2% in the wash water (e.g. at 0.15% concentration), a preferred detergent formulation containing sodium perborate tetrahydrate designed for use at 0.15% concentration in the wash water will therefore contain approximately 5 to 15% of that compound, corresponding roughly to 8 to 20 ppm 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 available oxygen present in the particular per-compound being used. For reactive aromatic mono-acyl compounds such as metachlorobenzoyldimethylhydantoin and metachlorobenzoylsuccinimide, strong bleaching is obtained when approximately equi-molecular 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-acetyl ethylenediamine, tetra-acetyl hydrazine and triacetyl cyanurate, the mole ratio of available oxygen to activator is preferably 2:1, although higher (e.g. 6:1) or lower (e.g. less than 1:1) mol ratios may be employed.

The enzyme concentration can be varied widely. Typically, the enzyme is present in amount in the range 0.001% to 4% by weight of the total detergent formulation, preferably in the range 0.05 to 1% and most preferably in the range 0.1 to 0.5%. The optimum proportion of enzyme to be used 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 an enzyme having an activity of about 1.5 Anson units per gram, a preferred range of proportions is one which gives 1 to 40 ppm, more preferably 2 to 8 ppm, of the enzyme in the wash water. This 2 to 8 ppm concentration corresponds to 0.003 to 0.012 Anson units per litre of wash water or, in a detergent formulation designed for use at a concentration of 1.5 gram per litre of wash water, about 0.002 to 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 detergent properties. Most preferred are those water-soluble surface-active compounds having anionic or nonionic properties. Anionic surface-active agents include those detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples of anionic solubilizing groups are sulphonate, sulphate, carboxylate and phosphate. Examples of suitable anionic detergents include soaps, such as 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. sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and sulphated and sulphonated synthetic detergents, particularly those having 8 to 26, and preferably 12 to 22, carbon atoms to the molecule.

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

Other deterative anionic surface-active agents which may be employed include olefin sulphonates, typically containing 8 to 25 carbon atoms; sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. coconut oil monoglyceride monosulphate, tallow diglyceride monosulphate; and hydroxy sulphonated higher fatty acid esters such as higher fatty acid esters of low molecular weight alkylol sulphonic acids, e.g. oleic acid ester of isethionic acid.

Suitable nonionic surface-active agents are those 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

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the polyhydration product thereof, polyethylene glycol.

- 5 As examples of suitable nonionic surface-active agents there may be noted condensation products of alkyl phenols with ethylene oxide, e.g., the reaction product of isooctyl phenol with 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 manitan monopalmitate and the condensation products of polypropylene glycol with ethylene oxide.

- 20 Cationic surface-active agents may also be employed. Suitable 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.

- 25 As examples of suitable synthetic cationic detergents there may be noted diamines such as those of the type



- wherein R is an alkyl group of 12 to 22 carbon atoms, e.g. N-aminoethyl stearyl amine and 30 N-aminoethyl myristyl amine; amide-linked amines such as those of the type



- wherein R' is an alkyl group of 12 to 18 carbon atoms, e.g. N-amino ethyl-stearyl amide and 35 N-amino ethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom is an alkyl group of 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 or methosulphate.
- 40 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 methosulphates and acetates.

- 45 The surface-active compounds which are preferred are those having anionic or nonionic properties. The most highly preferred water-soluble anionic detergent compounds are 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 higher alkyl benzene sulphonates,

higher alkyl sulphates and higher fatty acid monoglyceride sulphates.

- The surface-active agent is typically present in amount of 5 to 95% by weight of the detergent composition, preferably 10 to 25% by weight. 65

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

- In addition to the materials described above, the detergent composition 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. 70 75

The water-soluble inorganic builder salts may be suitable alkali metal, alkaline earth metal or heavy metal salts or mixtures thereof. Ammonium or an ethanalamine salt in a suitable amount may be added also, but generally the sodium and potassium salts are preferred. Examples are water-soluble sodium and potassium phosphates, silicates, carbonates, bicarbonates, borates, sulphates and chlorides. Particularly preferred builder salts are the alkaline builder salts such as polyphosphates, silicates and borates. 80 85

- 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 mixture of salts wherein the bicarbonate to tripolyphosphate ratio is in the range 1:1 to 3:1. 90 95

Both Phase I and Phase II sodium tripolyphosphate and mixtures thereof may be 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 to 95%, with small amounts, e.g. 4 to 13%, of other phosphates, e.g. pyrophosphate and orthophosphate. Sodium tripolyphosphate in its hydrated form may be used also, as may trisodium orthophosphate. 100 105

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. 110

Other suitable builder salts which may be present include the water-soluble sodium and potassium silicates, carbonates, borates, chlorides and sulphates. 115

Generally, when present the builder salt is employed in amount in the range 20 to 90%, preferably at least 25% (e.g. 35 to 80%) of the detergent composition. 120

The composition may also contain polymeric additives such as sodium carboxymethylcellulose or polyvinyl alcohol (e.g. in amount of 0.1 to 5%) or other polymeric 125

additives to inhibit redeposition of soil. Small amounts of optical brighteners may be present, as in proportions in the range 0.01 to 0.15%, examples of such brighteners are stilbene brighteners such as sodium-2-sulpho-4-(2-naphtho-1,2 triazole) stilbene; disodium 4,4'-bis (4-anilino-6-morpholino-s-triazin-2-yl-amino) stilbene disulphonate or disodium 4,4'-bis (4,6-dianilino-s-triazin-2-yl-amino) stilbenedisulphonate; and oxazole brighteners, having for example a 1-phenyl-2-benzoxazole ethylene structure. Perfumes, colouring agents and preservatives may also be included.

The activator, enzyme and per-compound may be added in powdered form to the other components of 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, e.g. separate packets (e.g. in moisture proof wrappings) of these ingredients may be supplied for addition to the wash water.

Thus, according to another aspect of the invention a process for removing stains from fabrics comprises subjecting the fabrics to water containing an enzyme, e.g. a proteolytic enzyme, and a per-compound, and preferably also an activator for the per-compound.

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 26.7 to 37.8°C, or in warm or hot water, e.g. at 43°, 49°, 60° or 71°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, e.g. for soaking several hours or overnight.

The following Examples illustrate the invention. In these examples, as in the rest of the specification, all proportions are by weight unless otherwise indicated.

EXAMPLE 1

(A) A detergent composition contained 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 subtilisin enzyme preparation known as "Alcalase" (trade mark); 16% of sodium perborate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$); 24% of meta-chlorobenzoyl-dimethylhydantoin (an activator for the perborate); the balance sodium sulphate (Na_2SO_4). In the composition the mol ratio of perborate to activator was about 1:1 (specifically it was 1.1:1).

The composition was used for the washing of standard cocoa-stained fabrics and standard coffee/tea-stained fabrics at 49°C for a period of 10 minutes, using 1 gram of the composition per litre of water in a Terg-O-Tometer. The effectiveness of the composition was determined by reflectance readings ("R_s") on the fabrics before and after washing, using a Gardner Colour Difference Meter for the measurement. The difference in reflectance before and after the washing is reported as "R_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 were 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 4/5 potassium dichloroisocyanurate ("KDCC") and 1/5 trichloroisocyanuric acid ("TCCA"). The results are tabulated below:

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Composition	A	B	C	D
Detergent	10%	10%	10%	10%
TPP	30%	30%	30%	30%
NTA	5%	5%	5%	5%
CMC	0.5%	0.5%	0.5%	0.5%
Subtilisin enzyme (Alcalase)	0.8%	—	0.8%	0.8%
Perborate	16%	—	—	—
Activator	24.8%	—	—	—
KDCC—TCCA	—	—	—	18.1%
Na ₂ SO ₄	Q.S.	Q.S.	Q.S.	Q.S.
R _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 was 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) was used with the enzyme the protein stain removal effectiveness dropped to below even the level obtained for the enzyme-free composition. The activator - perborate - enzyme composition was also highly effective for removal of coffee/tea stain.

EXAMPLE 2

In this Example an enzyme, sodium perborate and activator were dry-blended with a spray-dried detergent formulation having the following composition: sodium linear tridecylbenzenesulphonate 12.6% (active ingredient); sodium tallow alcohol sulphate 11.6% (active ingredient); TPP 35.8% sodium silicate (of 1:2.35 Na₂O:SiO₂ ratio) 6.3%; CMC 0.5%; polyvinyl alcohol 0.2%; water (including water of hydration) 8.9% Na₂SO₄, balance. Two blends were prepared, of the following compositions, in part by weight:

Composition	A	B
Spray dried detergent formulation	1.5	1.5
Subtilisin enzyme (Alcalase)	0.008	
Protease-Amylase (Monzyme)		0.002
Sodium perborate	0.16	0.16
Activator of Example 1	0.248	0.248

EXAMPLE 3

Examples 2 A and B were repeated except that the spray-dried detergent had a different composition and was made in the following manner: in a crutcher there were mixed in the order given 139 parts of water, 213 parts

of an aqueous slurry containing about 44% sodium linear tri - decylbenzenesulphonate, 109.3 parts of anhydrous sodium sulphate, 4.4 parts of borax, 0.13 part of phenolic anti-oxidant (Iphol 033), 71.4 parts of aqueous sodium silicate of 43.5% concentration (in

which the $\text{Na}_2\text{O}:\text{SiO}_2$ mol ratio is 1:2.35), and 157 parts of anhydrous pentasodium tripolyphosphate. The aqueous mixture was spray-dried to give a granular composition of the foregoing ingredients having a total mixture of about 8.5% (including water of hydration).

EXAMPLE 4

In this Example there were used compositions as described in Example 1A, except that the activator was (A) 11.9% of tetraacetyl ethylene diamine or (B) 10.4% tetraacetyl hydrazine, or (C) 13.3% triacetylcyanurate.

For comparison there were also used compositions (D) containing no activator and (E) containing no activator or perborate.

The compositions were used for the soaking of standard cocoa-stained and standard coffee/tea-stained fabrics, using 1 gram of the composition per litre of water. The water was initially at 49°C and cooled to room temperature (about 25°C) during the soaking period, which was 18 hours. The test fabrics were removed and dried and the R_d values were obtained.

The results are tabulated below:

Composition	A	B	C	D	E
Detergent	10%	10%	10%	10%	10%
TPP	30%	30%	30%	30%	30%
NTA	5%	5%	5%	5%	5%
CMC	0.5%	0.5%	0.5%	0.5%	0.5%
Subtilisin enzyme (Alcalase)	0.8%	0.8%	0.8%	0.8%	0.8%
Perborate	16%	16%	16%	16%	—
Perborate: activators mol ratio	2:1	3:1	2:1	no activator	—
NaSO_4	Q.S.	Q.S.	Q.S.	Q.S.	Q.S.
R_d					
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

These results indicate that the addition of the perborate to an enzyme-containing composition in a soaking test gave poorer results, both for the protein-containing stain and the coffee/tea stain, than when perborate was absent. The addition of the activator improved the stain removal not only for the coffee/tea stain but also for the protein stain.

A composition prepared as in Example 4A was storage tested by subjecting it for 3 days to a temperature of 49°C in a sealed container. During this period little, if any, undesirable odour developed. Soaking tests with standard cocoa-stained and coffee/tea-stained fabrics gave substantially identical results for the composition before the 3 day aging at 49°C and after such aging.

EXAMPLE 5

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

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

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

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

EXAMPLE 6

81.8 parts of a spray-dried built detergent formulation were mixed with 0.8 part of subtilisin enzyme, 7.4 parts of tetra acetyl ethylenediamine and 10 parts of sodium perborate. The spray-dried formulation contained 10.5% sodium linear tridecylbenzenesulphonate, 51% pentasodium tripolyphosphate, 6% sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ mol ratio 1:2.35), 8.5% sodium chloride, 13% sodium sulphate, 10% moisture (including water of hydration) and about 1% fluorescent brighteners.

The resulting composition was tested, using

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

The composition was also given a soaking test, as described in Example 4. The results, in terms of R_d , for the cocoa-stained and coffee/tea-stained fabrics were found to be substantially better than those for the same tests using the same composition except that no perborate or activator was present (these being replaced by an equal weight of sodium sulphate); the latter results were in turn substantially better than when the same composition was used without any enzyme, perborate or activator (these being replaced by an equal weight of sodium sulphate). In the same type of soaking test, made after the compositions had been aged for 3 days at 49°C in sealed containers, a similar superiority for the enzyme-containing composition with perborate plus activator was observed.

EXAMPLE 7

Example 1A was repeated, except that the composition contained 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 was repeated using, in place of the activator and perborate, 25% of solid m-chloroperbenzoic acid.

EXAMPLE 9

Example 4 was repeated, except that the amount of the perborate was 8% and the activator was m-chlorobenzoyl-dimethylhydantoin, present in amount of 13.9% (a 1:1 perborate:activator mol-ratio). R_d values of +15.4 (for cocoa-stained fabric) and +6.9 (for coffee/tea-stained fabric) were obtained.

The subtilisin enzyme "Alcalase" used in the foregoing Examples is characterized as having its maximum proteolytic activity at a pH of 8 to 9. This activity as measured on the commercial enzyme available from Novo Industrial A/S, Copenhagen, Denmark is about 1.5 Anson Units per gram of the enzyme. The commercial enzyme is a raw extract of bacillus subtilis culture and contains about 6% of pure crystallized proteolytic material.

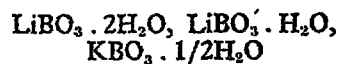
The "Monzyme" used in Examples 2 and

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 was 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, was 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



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.

Instead of using a combination of a per-salt such as a perborate and an activator, a percarboxylic (i.e. peroxy-carboxylic) acid, particularly a solid percarboxylic acid, or a salt of such acid, may be used. Among such percarboxylic acids are peroxybenzoic acids, particularly those having chloro or nitro substituents (e.g. m-chloroperoxybenzoic acid, as illustrated in Example 8 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 permissible 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, lyozyme, or glycosidases) or the lipases 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) Noval 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 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.
- 10 Minor amounts of these agents, e.g. 5%, 1% or less are effective.

WHAT WE CLAIM IS:—

1. A composition for use in washing stains from fabrics comprising an enzyme and a material which supplies a percarboxylic acid or salt thereof when the composition is added to the wash water.
2. A composition as claimed in Claim 1 in which the enzyme comprises a proteolytic enzyme.
3. A composition as claimed in Claim 1 or Claim 2 in which the said material comprises a per-salt and an activator therefor.
4. A composition as claimed in Claim 3 in which the per-salt is a perborate.
5. A composition as claimed in Claim 4 in which the perborate is sodium perborate.
6. A composition as claimed in any of Claims 3 to 5 in which the activator is a carboxylic ester activator, a carboxylic anhydride activator or a carboxylic acyl amide activator.
7. A composition as claimed in Claim 6 in which the activator is a benzoyl compound.
8. A composition as claimed in Claim 7 in which the activator is N-meta-chlorobenzoyl-5, 5-dimethylhydantoin.
9. A composition as claimed in Claim 6 in which the activator is a polyacyl amide.

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

11. A composition as claimed in Claim 10 in which the acyl groups are acetyl.

12. A composition as claimed in Claim 11 in which the activator is N,N,N',N'-tetraacetyl ethylene diamine.

13. A composition as claimed in any of Claims 3 to 12 containing substantially equimolar proportions of per-salt and activator.

14. A composition as claimed in Claim 1 or Claim 2 in which the said material is a chloroperoxybenzoic acid.

15. A composition as claimed in any of the preceding claims containing an organic surface-active detergent.

16. A composition as claimed in Claim 15 in which the detergent is nonionic.

17. A composition as claimed in Claim 15 in which the detergent is anionic.

18. A composition as claimed in any of Claims 15 to 17 containing a builder salt.

19. A composition as claimed in Claim 18 containing pentasodium tripolyphosphate and/or sodium nitrilotriacetate.

20. A composition as claimed in Claim 1 and substantially as described in any of the Examples.

21. A process for removing stains from fabrics which comprises subjecting the fabrics to water containing an enzyme and material as defined in any of claims 1 to 14.

22. A process as claimed in Claim 21 in which the enzyme is a proteolytic enzyme.

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3. A composition as claimed in Claim 1 or Claim 2 in which the said material comprises a per-salt and an activator therefor.
4. A composition as claimed in Claim 3 in which the per-salt is a perborate.
5. A composition as claimed in Claim 4 in which the perborate is sodium perborate.
6. A composition as claimed in any of Claims 3 to 5 in which the activator is a carboxylic ester activator, a carboxylic anhydride activator or a carboxylic acyl amide activator.
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9. A composition as claimed in Claim 6 in which the activator is a polyacyl amide.

10. A composition as claimed in Claim 6 in which the activator is a polyacyl amide having a pair of carboxylic acyl groups on a single nitrogen atom.
11. A composition as claimed in Claim 10 in which the acyl groups are acetyl.
12. A composition as claimed in Claim 11 in which the activator is N,N,N',N'-tetraacetyl ethylene diamine.
13. A composition as claimed in any of Claims 3 to 12 containing substantially equimolar proportions of per-salt and activator.
14. A composition as claimed in Claim 1 or Claim 2 in which the said material is a chloroperoxybenzoic acid.
15. A composition as claimed in any of the preceding claims containing an organic surface-active detergent.
16. A composition as claimed in Claim 15 in which the detergent is nonionic.
17. A composition as claimed in Claim 15 in which the detergent is anionic.
18. A composition as claimed in any of Claims 15 to 17 containing a builder salt.
19. A composition as claimed in Claim 18 containing pentasodium tripolyphosphate and/or sodium nitrilotriacetate.
20. A composition as claimed in Claim 1 and substantially as described in any of the Examples.
21. A process for removing stains from fabrics which comprises subjecting the fabrics to water containing an enzyme and material as defined in any of claims 1 to 14.
22. A process as claimed in Claim 21 in which the enzyme is a proteolytic enzyme.

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