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(54) **BLEACHING METHODS WITH PEROXYACID ACTIVATORS USED WITH ENZYMES**

BLEICHMETHODEN MIT PEROXYSÄURENAKTIVATOREN ZUSAMMEN MIT ENZYMEN

METHODES DE BLANCHIMENT AVEC DES ADJUVANTS AU PEROXYACIDE UTILISES AVEC
DES ENZYMES

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EP-A- 0 290 292	EP-A- 0 403 152
WO-A-94/10284	DE-A- 3 938 526

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EP 0 699 230 B1

DescriptionFIELD OF THE INVENTION

5 The present invention relates to methods of laundering which employ one or more types of detergent enzymes and a bleaching system with one or more bleach activators.

BACKGROUND OF THE INVENTION

10 Various types of detergent enzymes have long been conventionally used in laundry detergents to assist in the removal of certain stains from fabrics. These stains are typically associated with lipid and protein soils. The enzymes, however, have proven less effective against other types of soils and stains.

It has also long been known that peroxygen bleaches are effective for stain and/or soil removal from fabrics, but that such bleaches are temperature dependent. At a laundry liquor temperature of 60°C, peroxygen bleaches are only partially effective. As the laundry liquor temperature is lowered below 60°C, peroxygen bleaches become relatively ineffective. As a consequence, there has been a substantial amount of industrial research to develop bleaching systems which contain an activator that renders peroxygen bleaches effective at laundry liquor temperatures below 60°C.

15 Numerous substances have been disclosed in the art as effective bleach activators. One widely-used activator is tetraacetyl ethylene diamine (TAED). TAED provides effective hydrophilic cleaning especially on beverage stains, but has limited performance on dingy, yellow stains such as those resulting from body oils. Fortunately, another type of activator, such as nonanoyloxybenzenesulfonate (NOBS) and other activators which generally comprise long chain alkyl moieties, is hydrophobic in nature and provides excellent performance on dingy stains.

20 It would seem that a combination of enzymes with either hydrophilic or hydrophobic bleach activators, or both, would provide an effective "all-around" detergent composition which would perform well on most types of soils and stains. However, a hindrance to the development of such all-around cleaning compositions has been the discovery that many of the hydrophobic bleach activators developed thus far can promote damage to natural rubber parts used in certain washing machines. Because of the negative effects on washing machine parts, the selection of such detergent-added bleaching systems has been limited. This is especially true for European detergent/bleaches, since many washing machines manufactured in Europe are equipped with key parts, such as sump hoses and motor gaskets, made of natural rubber.

25 Another problem in developing an all-around cleaning composition has been finding a cleaning agent that is effective under heavy soil load conditions. The removal of heavy soil levels, especially nucleophilic and body soils, has proven especially difficult for conventional bleaching systems. Under such circumstances, conventional activators such as NOBS appear to interact with, and be destroyed by, heavy soil loads before they can optimally provide their intended bleaching function. Still another problem has been the stability of enzymes, especially lipases and proteases, in the presence of bleaches.

30 A need, therefore, exists for a method which provides effective cleaning performance over a wide variety of soils and stains. Moreover, the method should provide effective cleaning performance without substantially damaging natural rubber machine parts. In addition, the method should provide both bleaching performance and enzyme cleaning performance.

35 Without intending to be limited by theory, it is believed that typical hydrophobic bleach activators undergo a perhydrolysis reaction to form a peroxyacid bleaching agent. However, a typical by-product of the perhydrolysis reaction between conventional bleach activators and hydrogen peroxide is a diacylperoxide (DAP) species. Unfortunately, DAP species derived from hydrophobic activators tend to be insoluble, poorly dispersible, oily materials which form a residue which can deposit on the natural rubber machine parts that are exposed to the laundry liquor. The oily DAP residue can form a film on the natural rubber machine parts and promote free radical and peroxide damage to the rubber, which eventually leads to failure of the parts.

40 By the present invention, it has now been discovered that the class of hydrophobic bleach activators derived from amido acids forms hydrophobic amido peracids upon perhydrolysis without the production of harmful, oily DAP's. Again, while not intending to be limited by theory, it is believed that the DAP's produced by the perhydrolysis reaction of the amido acid-derived bleach activators used herein are insoluble crystalline solids. The solids do not form a coating film; therefore, the natural rubber parts are not exposed to the DAP's for extended periods of time and remain substantially undamaged.

45 In addition to the amido acid-derived bleach activators, it has also now been discovered that the class of bleach activators derived from N-acyl caprolactams provide both hydrophilic and hydrophobic bleaching action without the production of harmful DAP by-products.

50 Additionally, it has also now been discovered that the class of benzoxazintype bleach activators provide effective hydrophobic bleaching action without the production of harmful DAP by-products.

Surprisingly, it has also been discovered that certain enzymes, particularly lipase enzymes, are compatible with said classes of bleach activators.

Accordingly, the present invention solves the long-standing need for methods which provide efficient and effective performance over a wide range of cleaning needs by combining the cleaning actions of enzymes with the hydrophobic cleaning action of amido derived bleach activators or with the hydrophobic and hydrophilic cleaning action of N-acyl caprolactam bleach activators. The invention also provides efficient and effective methods for washing machines which have parts made of natural rubber, such that the natural rubber is substantially undamaged by the bleaching system. These and other benefits are secured by the invention, as will be seen hereinafter.

BACKGROUND ART

U.S. Patent 4,634,551, Burns et al, issued January 6, 1987, discloses amido peroxyacid bleaching compounds and their precursors which are employed in the present invention. See also, U.S. Patent 4,852,989, Burns et al, issued August 1, 1989. U.S. Patent 5,069,809, Lagerwaard et al, issued Dec. 3, 1991 discloses the combination of NOBS bleach activators with LIPOLASE, lipase enzymes. See E.P. Patent 341,947, Lagerwaard, et al, published November 15, 1989 for a discussion of the compatibility problems of lipase enzymes with certain bleaching systems. U.S. Patent 4,545,784, Sanderson, issued October 8, 1985, discloses the absorption of activators onto sodium perborate monohydrate.

EP-A-0170386 and EP-A-0290292 describe amido-derived bleach activators and its corresponding peracids. Enzymes such as proteases or amylases may also be included within the bleaching compositions.

DE-A-3938526 discloses benzoxazin bleach activators in washing and cleaning compositions which may contain, among various auxiliaries, enzymes.

EP-A-0122763 discloses bleach activators such as N-acetyl caprolactam adsorbed onto perborate. Enzymes can optionally be included within the compositions.

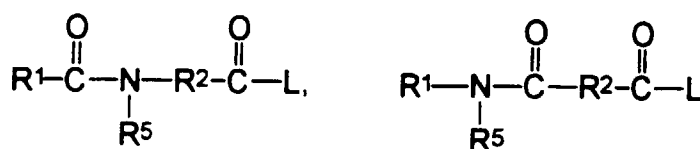
WO-A-94/10284 (54.3 document) discloses a granular detergent composition comprising an amido-derived bleach activator and a protease enzyme.

SUMMARY OF THE INVENTION

The invention herein provides methods which are safe for use in contact with natural rubber, and which provide not only bleach performance, but also good detergent enzyme stability and performance.

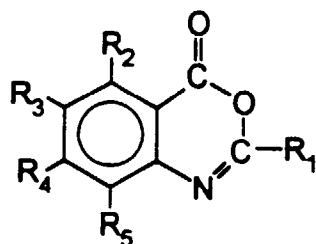
The present invention encompasses methods, which use compositions comprising an effective amount of one or more types of enzymes and a bleaching system comprising at least 0.1%, by weight, of a peroxygen bleaching compound and at least 0.1%, by weight, of one or more bleach activators, wherein said bleach activators are members selected from the group consisting of:

a) a bleach activator of the general formula:

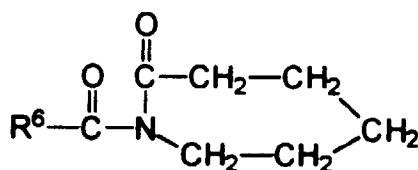


or mixtures thereof, wherein R¹ is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R² is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R⁵ is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is a leaving group;

b) benzoxazin-type bleach activators of the general formula:



wherein R_1 is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R_2 , R_3 , R_4 , and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkylamino, COOR_6 (wherein R_6 is H or an alkyl group) and carbonyl functions;
c) N-acyl caprolactam bleach activators of the formula:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons; and
d) mixtures of a), b) and c).

Preferably, the molar ratio of hydrogen peroxide yielded by the peroxygen bleaching compound to bleach activator is greater than 1.0. Most preferably, the molar ratio of hydrogen peroxide to bleach activator is at least 1.5.

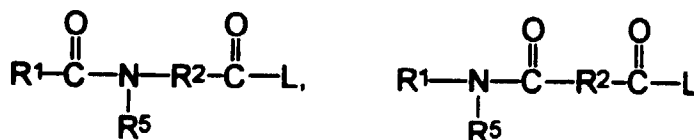
Preferred bleach activators of type a) are those wherein R^1 is an alkyl group containing from 6 to 12 carbon atoms, R^2 contains from 1 to 8 carbon atoms, and R^5 is H or methyl. Particularly preferred bleach activators are those of the above general formulas wherein R^1 is an alkyl group containing from 7 to 10 carbon atoms and R^2 contains from 4 to 5 carbon atoms.

Preferred bleach activators of type b) are those wherein R_2 , R_3 , R_4 , and R_5 are H and R_1 is a phenyl group.

The preferred acyl moieties of said N-acyl caprolactam bleach activators of type c) have the formula $R^6\text{-CO-}$ wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R^6 is a member selected from the group consisting of phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

Other highly preferred methods use detergent compositions comprising bleach activators selected from the group consisting of:

a) a bleach activator of the formula:



or mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^2 is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R^5 is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is a leaving group;

b) a N-acyl caprolactam bleach activator of the formula:



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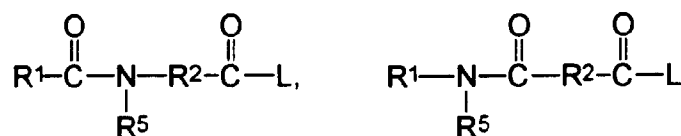
It is also believed that the bleach activators within the invention can render peroxygen bleaches more efficient even at laundry liquor temperatures wherein bleach activators are not necessary to activate the bleach, i.e., above

about 60°C. Therefore, with bleach systems of the invention, less peroxygen bleach is required to get the same level of surface bleaching performance as is obtained with the peroxygen bleach alone.

The bleaching systems, wherein the bleach activator is used, also have as an essential component a peroxygen bleach capable of releasing hydrogen peroxide in aqueous solution.

The Bleach Activator

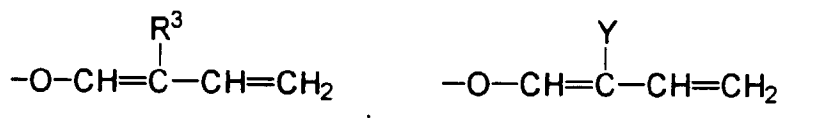
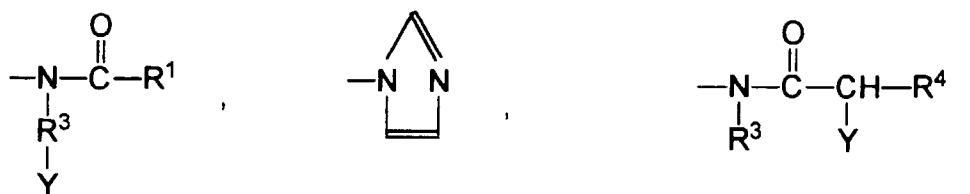
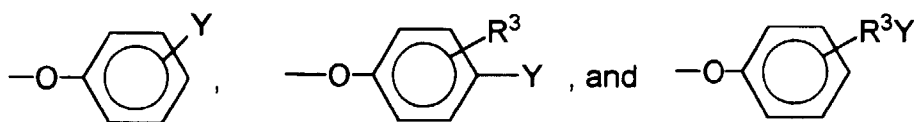
Amido Derived Bleach Activators - The bleach activators of type a) employed in the present invention are amide substituted compounds of the general formulas:

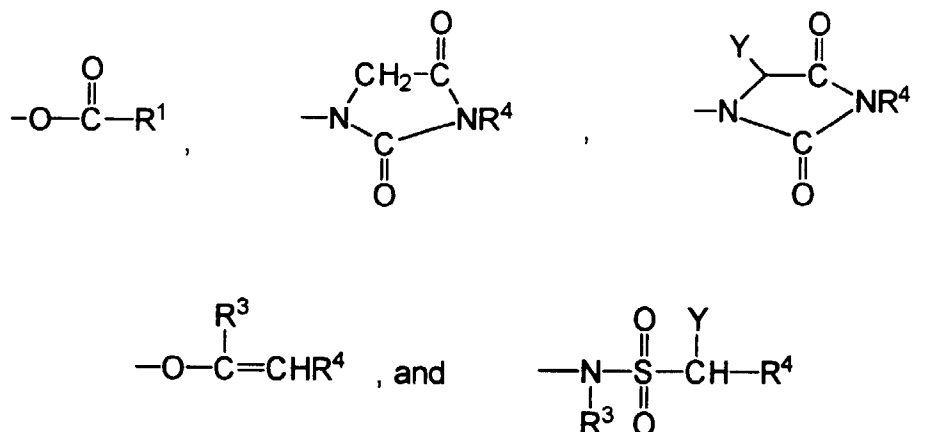


or mixtures thereof, wherein R¹, R² and R⁵ are as defined above and L can be essentially any suitable leaving group. A leaving group is any group that is displaced from the bleaching activator as a consequence of the nucleophilic attack on the bleach activator by the perhydroxide anion. This, the perhydrolysis reaction, results in the formation of the peroxycarboxylic acid. Generally, for a group to be a suitable leaving group it must exert an electron attracting effect. It should also form a stable entity so that the rate of the back reaction is negligible. This facilitates the nucleophilic attack by the perhydroxide anion.

The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behavior are those in which their conjugate acid has a pKa in the range of from 4 to 13, preferably from about 6 to about 11 and most preferably from 8 to 11.

Preferred bleach activators are those of the above general formula wherein R¹, R² and R⁵ are as hereinabove defined and L is selected from the group consisting of:

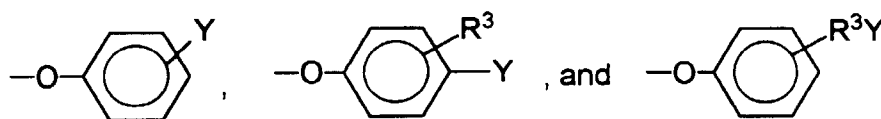




and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group.

The preferred solubilizing groups are $\text{---SO}_3^-\text{M}^+$, $\text{---CO}_2^-\text{M}^+$, $\text{---SO}_4^-\text{M}^+$, $\text{---N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}=\text{N}(\text{R}^3)_3$ and most preferably $\text{---SO}_3^-\text{M}^+$ and $\text{---CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.

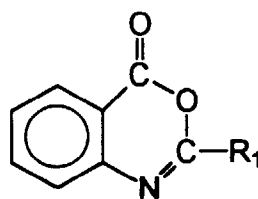
Preferred bleach activators are those of the above general formula wherein L is selected from the group consisting of:



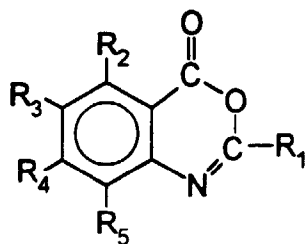
wherein R^3 is as defined above and Y is $\text{---SO}_3^-\text{M}^+$ or $\text{---CO}_2^-\text{M}^+$ wherein M is as defined above.

Another important class of bleach activators, including those of type b) and type c), provide organic peracids as described herein by ring-opening as a consequence of the nucleophilic attack on the carbonyl carbon of the cyclic ring by the perhydroxide anion. For instance, this ring-opening reaction in type c) activators involves attack at the caprolactam ring carbonyl by hydrogen peroxide or its anion. Since attack of an acyl caprolactam by hydrogen peroxide or its anion occurs preferably at the exocyclic carbonyl, obtaining a significant fraction of ring-opening may require a catalyst. Another example of ring-opening bleach activators can be found in type b) activators, such as those disclosed in U.S. Patent 4,966,723, Hodge et al, issued Oct. 30, 1990.

Such activator compounds disclosed by Hodge include the activators of the benzoxazin-type, having the formula:

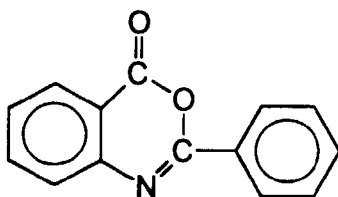


including the substituted benzoxazins of the type



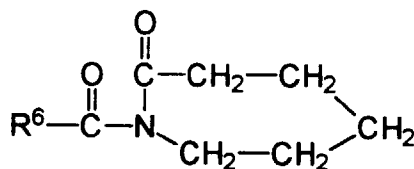
wherein R_1 is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R_2 , R_3 , R_4 , and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkyl amino, COOR_6 (wherein R_6 is H or an alkyl group) and carbonyl functions.

A preferred activator of the benzoxazin-type is:



When the activators are used, optimum surface bleaching performance is obtained with washing solutions wherein the pH of such solution is between 8.5 and 10.5 and preferably between 9.5 and 10.5 in order to facilitate the perhydrolysis reaction. Such pH can be obtained with substances commonly known as buffering agents, which are optional components of the bleaching systems herein.

The N-Acyl Caprolactam Bleach Activators - The N-acyl caprolactam bleach activators of type c) employed in the present invention have the formula:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons. Caprolactam activators wherein the R^6 moiety contains at least 6, preferably from 6 to 12, carbon atoms provide hydrophobic bleaching which affords nucleophilic and body soil clean-up, as noted above. Caprolactam activators wherein R^6 comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of hydrophobic and hydrophilic caprolactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Highly preferred N-acyl caprolactams are selected from the group consisting of benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, and mixtures thereof.

Methods for making N-acyl caprolactams are well known in the art. Examples I and II, included below, illustrate preferred laboratory syntheses.

Contrary to the teachings of U.S. Pat. 4,545,784, cited above, the bleach activator is preferably not absorbed onto the peroxygen bleaching compound. To do so in the presence of other organic detergent ingredients could cause safety problems.

The bleach activators of type a), b) or c) will comprise at least 0.1%, preferably from 0.1% to 50%, more preferably from 1% to 30%, most preferably from 3% to 25%, by weight of bleaching system or detergent composition.

When the activators are used, optimum surface bleaching performance is obtained with washing solutions wherein the pH of such solution is between 8.5 and 10.5 and preferably between 9.5 and 10.5 in order to facilitate the perhydrolysis reaction. Such pH can be obtained with substances commonly known as buffering agents, which are optional

components of the bleaching systems herein.

The Peroxygen Bleaching Compound

The peroxygen bleaching systems useful herein are those capable of yielding hydrogen peroxide in an aqueous liquor. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or more such bleaching compounds can also be used, if desired.

Preferred peroxygen bleaching compounds include sodium perborate, commercially available in the form of mono-, tri-, and tetra-hydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium percarbonate, and sodium peroxide. Particularly preferred are sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate. Percarbonate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching liquor. It is believed that such rapid dissolution results in the formation of higher levels of percarboxylic acid and, thus, enhanced surface bleaching performance.

Highly preferred percarbonate can be in uncoated or coated form. The average particle size of uncoated percarbonate ranges from 400 to 1200 microns, most preferably from 400 to 600 microns. If coated percarbonate is used, the preferred coating materials include mixtures of carbonate and sulphate, silicate, borosilicate, or fatty carboxylic acids.

The peroxygen bleaching compound will comprise at least 0.1%, preferably from 1% to 75%, more preferably from 3% to 40%, most preferably from 3% to 25%, by weight of bleaching system or detergent composition.

The weight ratio of bleach activator to peroxygen bleaching compound in the bleaching system typically ranges from 2:1 to 1:5. Preferred ratios range from 1:1 to 1:3.

The bleach activator/bleaching compound systems herein are useful per se as bleaches. However, such bleaching systems are especially useful compositions which can comprise various deterative adjuncts such as surfactants and builders.

The Deterative Enzymes

The deterative enzymes of the present invention are included for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of fugitive dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to 50 mg by weight, more typically 0.01 mg to 10 mg, of active enzyme per gram of detergent composition. Stated otherwise, an effective amount of the enzymes employed in the present invention will comprise at least 0.001%, preferably from 0.001% to 5%, more preferably from 0.001% to 1%, most preferably from 0.01% to 1%, by weight of detergent composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B.subtilis*, *B.lentus* and *B.licheniformis*. Another suitable protease is a modified bacterial serine protease enzyme obtained from *Bacillus subtilis* or *Bacillus licheniformis*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Most preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus*, particularly *Bacillus lentus*, in which arginine replaced lysine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958.4, U.S. Patent No. 5,185,250 and U.S. Patent No. 5,204,015. Genetically modified variants, particularly of Protease C, are also included herein.

Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have

a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53-20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLEASE enzyme, derived from the fungus *Humicola lanuginosa* and expressed in *Aspergillus oryzae* as host and commercially available from Novo (see also E.P. Patent 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 4,261,868, issued April 14, 1981 to Horn, et al, U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0199405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319, and 3,519,570.

Enzyme Stabilizers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium ions in the finished compositions which provide calcium ions to the enzymes. Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706, cited above. Typical detergents, especially liquids, will comprise from 1 to 30, preferably from 2 to 20, more preferably from 5 to 15, and most preferably from 8 to 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium ions. The level of calcium ion should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium salt can be used as the source of calcium ion, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium hydroxide, calcium formate, and calcium acetate. A small amount of calcium ion, generally from 0.05 to 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

The compositions herein may also optionally, but preferably, contain various additional stabilizers including silicate coatings and, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from 0.25% to 10%, preferably from 0.5% to 5%, more preferably from 0.75% to 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

Detersive Surfactant

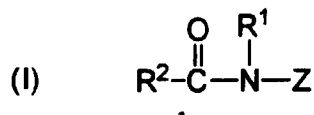
The amount of detersive surfactant included in the fully-formulated detergent compositions used according to the present invention can vary from 1% to 99.8% depending upon the particular surfactants used and the effects desired. Preferably, the detersive surfactants comprise from 5% to 80% by weight of the detergent ingredients.

The detersive surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Preferred detergent compositions comprise anionic detersive surfactants or mixtures of anionic

surfactants with other surfactants, especially nonionic surfactants.

Nonlimiting examples of surfactants useful herein include the conventional C₁₁-C₁₈ alkyl benzene sulfonates and primary, secondary, and random alkyl sulfates, the C₁₀-C₁₈ alkyl alkoxy sulfates, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, C₁₂-C₁₈ alpha-sulfonated fatty acid esters, C₁₂-C₁₈ alkyl and alkyl phenol alkoxyates (especially ethoxyates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

One particular class of adjunct nonionic surfactants especially useful herein comprises the polyhydroxy fatty acid amides of the formula:



wherein: R¹ is H, C₁-C₈ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₅-C₃₂ hydrocarbyl moiety, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₉ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glyceryl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂(CHOR') (CHOH)-CH₂OH, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxyated derivatives thereof. Most preferred are glyceryls wherein n is 4, particularly -CH₂-(CHOH)₄CH₂OH.

In Formula (I), R¹ can be, for example, N-methyl, N-ethyl, N-propyl, Nisopropyl, N-butyl, N-isobutyl, N-2-hydroxyethyl, or N-2-hydroxy propyl. For highest sudsing, R¹ is preferably methyl or hydroxyalkyl. If lower sudsing is desired, R¹ is preferably C₂-C₈ alkyl, especially n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Deterative Builders

Optional detergent ingredients employed in the present invention contain inorganic and/or organic deterative builders to assist in mineral hardness control. If used, these builders comprise from 5% to 80% by weight of the detergent compositions.

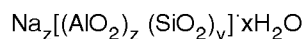
Inorganic deterative builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, nonphosphate builders are required in some locales.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, available from Hoechst under the trademark "SKS"; SKS-6 is an especially preferred layered silicate builder.

Carbonate builders, especially a finely ground calcium carbonate with surface area greater than 10 m²/g, are preferred builders that can be used in granular compositions. The density of such alkali metal carbonate built detergents can be in the range of 450-850 g/l with the moisture content preferably below 4%.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are especially useful in the present invention. Preferred aluminosilicates are zeolite builders which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. Methods for producing aluminosilicate ion exchange materials are disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976, and U.S. Patent 4,605,509, Corkill, et al, issued Aug. 12, 1986. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B) (including those disclosed in EPO 384,070), and Zeolite X. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds, such as ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergent builders include the ether hydroxy-polycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyl-oxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are preferred polycarboxylate builders that can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Optional Detergent Adjuncts

As a preferred embodiment, the conventional detergent ingredients employed herein can be selected from typical detergent composition components such as detergent surfactants and detergent builders. Optionally, the detergent ingredients can include one or more other detergent adjuncts or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual detergent adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al, are incorporated herein by reference. Such adjuncts which can be included in detergent compositions employed in the present invention, in their conventional art-established levels for use (generally from 0% to 20% of the detergent ingredients, preferably from 0.5% to 10%), include color speckles, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, perfumes, solvents, solubilizing agents, clay soil removal/anti-redeposition agents, polymeric dispersing agents, processing aids, fabric softening components and static control agents.

Bleach systems optionally, but preferably, will also comprise a chelant which not only enhances bleach stability by scavenging heavy metal ions which tend to decompose bleaches, but also assists in the removal of polyphenolic stains such as tea stains, and the like. Various chelants, including the aminophosphonates, available as DEQUEST from Monsanto, the nitrilotriacetates, the hydroxyethyl-ethylenediamine triacetates, and the like, are known for such use. Preferred biodegradable, non-phosphorus chelants include ethylene-diamine disuccinate ("EDDS"; see U.S. Patent 4,704,233, Hartman and Perkins), ethylenediamine-N,N'-diglutamate (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinate (HPDDS) compounds. Such chelants can be used in their alkali or alkaline earth metal salts, typically at levels from 0.1% to 10% of the present compositions.

Optionally, the detergent compositions employed herein can comprise, in addition to the bleaching system of the present invention, one or more other conventional bleaching agents, activators, or stabilizers which do not react with or otherwise harm natural rubber. In general, the formulator will ensure that the bleach compounds used are compatible with the detergent formulation. Conventional tests, such as tests of bleach activity on storage in the presence of the separate or fully-formulated ingredients, can be used for this purpose. A specific example of an optional bleaching agent for incorporation in this invention is tetraacetyl ethylene diamine (TAED). Such bleaching compounds and agents

can be optionally included in detergent compositions in their conventional art-established levels of use, generally from 0% to 15%, by weight of detergent composition.

Bleaching activators of the invention are especially useful in conventional laundry detergent compositions such as those typically found in granular detergents or laundry bars. U.S. Patent 3,178,370, Okenfuss, issued April 13, 1965, describes laundry detergent bars and processes for making them. Philippine Patent 13,778, Anderson, issued Sept. 23, 1980, describes synthetic detergent laundry bars. Methods for making laundry detergent bars by various extrusion methods are well known in the art.

The following examples are given to further illustrate the present invention, but are not intended to be limiting thereof.

EXAMPLE I

Synthesis of Nonanoyl Caprolactam - To a two litre three necked round bottomed flask equipped with a condenser, overhead stirrer and 250ml addition funnel is charged 56.6g (0.5 moles) caprolactam, 55.7g (0.55 moles) triethylamine and 1 litre of dioxane; the resulting solution is heated to reflux (120°C). A solution of 88.4g (0.5 moles) nonanoyl chloride dissolved in 200ml of dioxane is then added over 30 minutes and the mixture is refluxed for a further 6 hours. The reaction mixture is then cooled, filtered, and the solvent removed by rotary evaporation to yield 120.5g of the product as a dark oil. This crude product is then dissolved in diethyl ether, washed with 3x50ml aliquots of water, dried over magnesium sulphate and the solvent removed by rotary evaporation to yield 81.84g (65% theoretical yield) of product which is shown by NMR to be 90% pure, with the remaining material being nonanoic acid.

EXAMPLE II

Synthesis of Benzoyl Caprolactam - To a two litre three necked round bottomed flask equipped with a condenser, overhead stirrer and 250ml addition funnel is charged 68.2g (0.6 moles) caprolactam, 70g (0.7 moles) triethylamine and 1 litre of dioxane; the resulting solution is heated to reflux (120°C). A solution of 84.4g (0.6 moles) benzoyl chloride dissolved in 200ml of dioxane is then added over 30 minutes and the mixture is refluxed for a further 6 hours. The reaction mixture is then cooled, filtered, and the solvent removed by rotary evaporation to yield 121.7g of the product as an oil which crystallizes on standing. This crude product is then redissolved in toluene and precipitated with hexane, yielding 103g (79% theoretical yield) of a white solid which is shown by NMR to be over 95% pure, with the remaining material being benzoic acid.

EXAMPLE III

Synthesis of (6-nonanamidocaproyl)oxybenzenesulfonate (NACA-OBS).

6-nonanamidocaproic Acid (NACA) - The reaction is carried out in a 12L 3-necked flask equipped with a thermometer, addition funnel and mechanical stirrer. To a solution made from 212g (5.3 moles) of sodium hydroxide and 6L of water (cooled to room temperature) is added 694.3g (5.3 moles) of 6-aminocaproic acid. This mixture is cooled to 10°C and a solution of 694.3g (5.3 moles) of nonanoyl chloride in 1L of ether is added in a slow stream (about 2.5 hours) keeping the temperature at 10-15°C. During the addition, and subsequently until acidification, the reaction is maintained at pH 11-12 by periodic addition of 50% NaOH. After the addition is complete, the reaction is stirred for another 2 hours at 10°C and allowed to come to room temperature before acidification to pH 1 with conc. HCl. The precipitated product is vacuum filtered, the filter cake is washed twice with 8L portions of water and the product air dried overnight. It is then suspended in 3L of hexane, filtered and washed with an additional 3L of hexane. The product is then vacuum dried overnight (50°C, 1 mm) to give 1354 g (94%) of NACA.

Acid Chloride (NACA-Cl) - The reaction is carried out in a 5L, 3-necked flask equipped with an addition funnel, mechanical stirrer and argon sweep. To a suspension of 542g (2.0 moles) of NACA in 2L of toluene is added (in a slow stream over 30 minutes) 476g (4.0 moles) of thionyl chloride. This mixture is stirred at room temperature for four hours during which time the solids dissolve. The solution is partially evaporated (30°C, 10 mm) to remove any excess thionyl chloride leaving 905g of NACA-Cl/toluene solution (contains approximately 2 moles of NACA-Cl). An IR spectrum confirms conversion of COOH to COCl.

(6-nonanamidocaproyl)oxybenzenesulfonate (NACA-OBS) - The reactor is a 12L, 3-necked flask equipped with a condenser, mechanical stirrer and static argon supply. To the reactor are added 647g of the above NACA-Cl/toluene solution (1.43 moles), 6L of toluene and 310.8g (1.43 moles) of disodium p-phenolsulfonate (disodium p-phenolsulfonate is previously prepared and dried in a vacuum oven before use (110°C, 0.1mm hg, 18 hours). This mixture is refluxed for 18 hours. After cooling to room temperature, the product is collected on a Buchner funnel and dried to give 725g of crude solids. The crude is taken up in 7L of refluxing 87:13 (v,v) methanol/water, filtered hot and allowed to

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recrystallize at room temperature. The resulting precipitate is filtered and vacuum dried (50°C, 0.1 mm) for 18 hours to give 410g (64% based on NACA) of light tan product. A trace of unreacted phenolsulfonate is indicated by the small doublets at 6.75 and 7.55 ppm in the ¹H spectrum. Otherwise, the spectra are consistent with expected structure and no other impurities are evident.

EXAMPLE IV

A granular detergent composition is prepared comprising the following ingredients.

Component	Weight %
C ₁₂ linear alkyl benzene sulfonate	22
Phosphate (as sodium tripolyphosphate)	30
Sodium carbonate	14
Sodium silicate	3
Lipase	0.3
Sodium percarbonate	5
Ethylenediamine disuccinate chelant (EDDS)	0.4
Sodium sulfate	5.5
Nonanoyl caprolactam	5
Filler* and water	Balance to 100%

*Can be selected from convenient materials such as CaCO₃, talc, clay, silicates, and the like.

In testing the bleaching performance and effect on natural rubber washing machine parts, the following test method is used:

Aqueous crutcher mixes of heat and alkali stable components of the detergent compositions are prepared and spray-dried and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown.

The detergent granules with bleach activator are added together with 5 lb. (2.3 kg) of previously laundered fabrics including natural rubber articles such as elastic materials, to an automatic washing machine equipped with a natural rubber sump hose. Actual weights of detergent and bleach activator are taken to provide a 950 ppm concentration of the former and 50 ppm concentration of the latter in the 17 gallon (65 l) water-fill machine. The water used has 119.8 mg/liter (7 grains/gallon) hardness and a pH of 7 to 7.5 prior to (about 9 to about 10.5 after) addition of the detergent and bleaching system.

The fabrics are laundered at 35°C (95°F) for a full cycle (12 min.) and rinsed at 21°C (70°F). The laundering method is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts or without damage to the natural rubber contained in the fabrics and with good enzyme performance.

EXAMPLE V

A granular detergent composition is prepared comprising the following ingredients.

Component	Weight %
Anionic alkyl sulfate	7
Nonionic surfactant	5
Zeolite (0.1-10 micron)	10
Trisodium citrate	2
SKS-6 silicate builder	10
Acrylate maleate polymer	4
Nonanoyl caprolactam	5
Sodium percarbonate*	15
Sodium carbonate	5
Ethylenediamine disuccinate chelant (EDDS)	0.4
Suds suppressor	2
Protease (as SAVINASE)	0.3

*Average particle size of 400 to 1200 microns.

(continued)

Component	Weight %
Lipase (as LIPOLASE)	0.3
Soil release agent	0.2
Minors, filler** and water	Balance to 100%

**Can be selected from convenient materials such as CaCO₃, talc, clay, silicates, and the like.

In testing the bleaching performance and effect on natural rubber washing machine parts, the following test method is used:

Aqueous crutcher mixes of heat and alkali stable components of the detergent composition are prepared and spray-dried, and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown.

The detergent granules with bleach activator are added via the dispensing drawer together with 5 lb. (2.3 kg) of previously laundered fabrics to an automatic washing machine equipped with a natural rubber sump hose. Actual weights of detergent and bleach activator are taken to provide a 8,000 ppm concentration of the former and 400 ppm concentration of the latter in the 17 l water-fill machine. The water used has 10 grains/gallon hardness and a pH of 7 to 7.5 prior to (about 9 to about 10.5 after) addition of the detergent and bleaching system.

The fabrics are laundered at 40°C (104°F) for a full cycle (40 min.) and rinsed at 21°C (70°F). The laundering method is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE VI

A detergent composition is prepared by a procedure identical to that of Example V, with the single exception that an equivalent amount of benzoyloxybenzene sulfonate is substituted for the nonanoyl caprolactam. The laundering method of Example V is repeated for about 1200 cycles at which time the natural rubber parts ruptures.

EXAMPLE VII

A detergent composition is prepared by a procedure identical to that of Example V, with the single exception that an equivalent amount of (6-nonanamidocaproyl)-oxybenzenesulfonate as prepared in Example III is substituted for the nonanoyl caprolactam. The laundering method of Example V is repeated for 2000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE VIII

A detergent composition is prepared by a procedure identical to that of Example V, with the exceptions that 15% of a 1:1:1 mixture of benzoyl caprolactam, nonanoyl caprolactam and (6-nonanamidocaproyl)oxybenzene-sulfonate as prepared following Example III is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE IX

A detergent composition is prepared by a procedure identical to that of Example IV, with the exceptions that 20% of a 1:1 mixture of benzoyl caprolactam and (6-nonanamidocaproyl)oxybenzenesulfonate as prepared following Example III is substituted for the nonanoyl caprolactam, the amount of sodium percarbonate is 20%, and the amount of phosphate is 0%. The laundering method of Example IV is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE X

A detergent composition is prepared by a procedure identical to that of Example V, with the single exception that an equivalent amount of a benzoxazin-type activator is substituted for the nonanoyl caprolactam. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XI

A detergent composition is prepared by a procedure identical to that of Example V, with the exceptions that 10% of a 1:1 mixture of a benzoxazin-type activator and tetraacetyl ethylene diamine is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 25%. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XII

A laundry bar suitable for hand-washing soiled fabrics is prepared by standard extrusion processes and comprises the following:

Component	Weight %
C ₁₂ linear alkyl benzene sulfonate	30
Phosphate (as sodium tripolyphosphate)	7
Sodium carbonate	25
Sodium pyrophosphate	7
Coconut monoethanolamide	2
Zeolite A (0.1-10 micron)	5
Carboxymethylcellulose	0.2
Polyacrylate (m.w. 1400)	0.2
(6-nonanamidocaproyl)oxybenzenesulfonate	5
Sodium percarbonate	5
Brightener, perfume	0.2
Protease (as Protease C)	0.3
Lipase (as LIPOLASE)	0.3
CaSO ₄	1
MgSO ₄	1
Water	4
Filler*	Balance to 100%

*Can be selected from convenient materials such as CaCO₃, talc, clay, silicates, and the like.

The detergent laundry bars are processed in conventional soap or detergent bar making equipment as commonly used in the art. Testing is conducted following the procedures and methods in Example V. The laundering method, is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XIII

A detergent composition is prepared by a procedure identical to that of Example XII, with the single exception that an equivalent amount of benzoyl caprolactam is substituted for the (6-nonanamidocaproyl)oxybenzenesulfonate. The laundering method of Example XII is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XIV

A detergent composition is prepared by a procedure identical to that of Example XII, with the single exception that an equivalent amount of nonanoyl caprolactam is substituted for the (6-nonanamidocaproyl)oxybenzenesulfonate. The laundering method of Example XII is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XV

A granular detergent composition is prepared comprising the following ingredients.

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Component	Weight %
Anionic alkyl sulfate	7
Nonionic surfactant	5
Zeolite (0.1-10 micron)	10
Trisodium citrate	2
SKS-6 silicate builder	10
Acrylate maleate polymer	4
Nonanoyl caprolactam	5
Sodium percarbonate*	15
Sodium carbonate	5
Ethylenediamine disuccinate chelant (EDDS)	0.4
Suds suppressor	2
Protease (as Protease C)	0.5
Soil release agent	0.2
Minors, filler** and water	Balance to 100%

*Average particle size of 400 to 1200 microns.

**Can be selected from convenient materials such as CaCO_3 , talc, clay, silicates, and the like

Aqueous crutcher mixes of heat and alkali stable components of the detergent composition are prepared and spray-dried, and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown.

Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XVI

A detergent composition is prepared by a procedure identical to that of Example XV, with the single exception that an equivalent amount of benzoyl caprolactam is substituted for the nonanoyl caprolactam.

Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XVII

A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of (6-nonanamidocaproyl)oxybenzenesulfonate is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XVIII

A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of a 1:1 mixture of (6-nonanamidocaproyl)oxybenzenesulfonate and (6-decanamidocaproyl)oxybenzenesulfonate activator is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XIX

A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of a 1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate and (6-decanamidocaproyl)oxybenzenesulfonate activator is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

5 EXAMPLE XX

A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of (6-octanamidocaproyl)oxybenzenesulfonate is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

10 Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

EXAMPLE XXI

15 A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of (6-decanamidocaproyl)oxybenzenesulfonate activator is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

20 Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant to, the natural rubber parts and with good enzyme stability and performance.

Method of Processing the Bleach Activators

25 The bleach activators may be processed with a range of organic and inorganic substances to achieve a rapid dispersion in the bleaching liquor and to insure good stability in the detergent composition. The bleach activators are preferably employed in particulate form.

30 An example of preferred caprolactam bleach activator particles is an agglomerate of 65%, by weight, benzoyl caprolactam; 7% of a builder, such as aluminium silicate; 15% sodium carbonate; 9% dispersant, such as a polyacrylate polymer; and 4% of a solubilizing agent, such as a linear alkyl sulfonate. Another example of a preferred caprolactam bleach activator particle is an agglomerate of 80% to 85%, by weight, benzoyl caprolactam and 15% to 20% of a binder, such as tallow alcohol ethoxylate, preferably TAE25.

35 An example of a preferred amido-derived bleach activator particle comprises a 1:1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzenesulfonate, and citric acid powder. The mixture is intimately mixed in a food mixer for 5-10 minutes. To the resultant mixture is added tallow alcohol ethoxylate (TAE25) nonionic surfactant at 50° C until granules are formed. Typically successful granulations are achieved with a ratio of bleach activator/citric acid solid mixtures:nonionic binding agent of 3.5:1. The resultant granules, ellipsoidal and spherical in shape, are white and free flowing.

40 A typical particle composition is 40% to 60%, preferably 55%, by weight, of the bleach activator or mixture of bleach activators; 20% to 40%, preferably 25%, by weight, of citric acid; and 15% to about 30%, preferably 20%, by weight, TAE25 binding agent. Alternatively, a 2:1 mixture of (6-decanamidocaproyl)oxybenzenesulfonate and citric acid powder may be used. In this case, the composition on the granule is 55% bleach activator, 25% citric acid, and 20% TAE25 binding agent. Other preferred organic binding agents include anionic surfactants (C₁₂ linear alkyl benzene sulfonates), polyethylene glycols, and TAE50.

45 Another example of a preferred amido-derived bleach activator particle comprises a 1:1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and sodium hydrogen sulfate. To the mixture is added 20% by weight of an anionic surfactant (alkyl sulfate is particularly preferred). The components are mixed into a paste with water, typically 30-50% by weight of water being added, and introduced into an air flow such that droplets are formed. This technique is commonly known as spray drying. This may be achieved using, for example
50 a Nyro atomiser, or a spray gun. Hot air (typically 150-300 degree Celisius) is blasted upwards through a column. The resulting particles formed are collected at the bottom of the column and classified into desired size.

55 A typical particle composition is 40-60%, preferably 55%, by weight of the bleach activator or mixture of activators, 20-40%, preferably 25%, of sodium hydrogen sulfate, and 15-25%, preferably about 20%, of anionic surfactant. Alternatively, a 2:1 mixture of (6-decanamidocaproyl)oxybenzenesulfonate and sodium hydrogen sulfate may be used. Citric acid or boric acid may also be used in place of sodium hydrogen sulfate in the above examples.

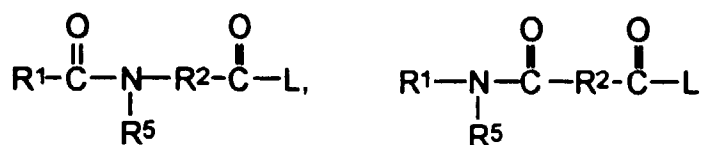
The particle size of the resulting granules may be varied according to the desired performance/stability. Fine particles (<250 µm) show improved solubility; though coarse particles (>1180 µm) are more stable in high temperatures/moist environments. A typical, preferred particle size range is 250-1180 µm; particles conforming to this specification

show excellent stability and solubility.

Claims

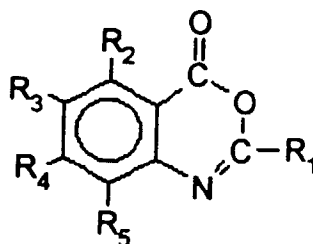
1. A method for cleaning fabrics in an automatic washing machine having parts made of natural rubber which is susceptible to oxidative degradation, said method comprising agitating said fabrics in said machine in an aqueous liquor comprising a detergent composition comprising an effective amount of one or more types of enzymes and a bleaching system comprising at least 0.1% by weight of a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous liquor and at least 0.1% by weight of one or more bleach activators, wherein said bleach activators are members selected from the group consisting of :

a) a bleach activator of the general formula :



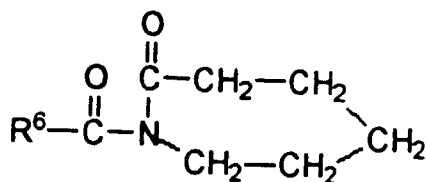
or mixtures thereof, wherein R¹ is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R² is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R⁵ is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is a leaving group;

b) a benzoxazin-type bleach activator of the formula :



wherein R₁ is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R₂, R₃, R₄, and R₅ may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxyl, amino, alkylamino, -COOR₆, wherein R₆ is H or an alkyl group and carbonyl functions;

c) a N-acyl caprolactam bleach activator of the formula :



wherein R₆ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons; and

d) mixtures of a), b) and c).

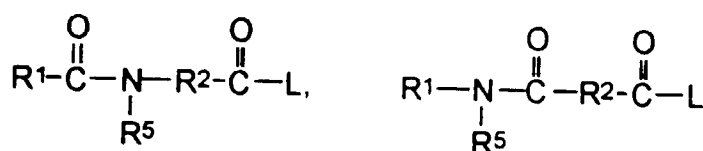
2. A method according to Claim 1 wherein said enzymes comprise at least 0.001%, by weight of said detergent

composition, and are selected from the group consisting of proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof.

3. A method according to Claim 2 wherein said enzyme is lipase derived from the fungus Humicola lanuginosa or a modified bacterial serine protease derived from Bacillus subtilis, Bacillus lentus, or Bacillus licheniformis.

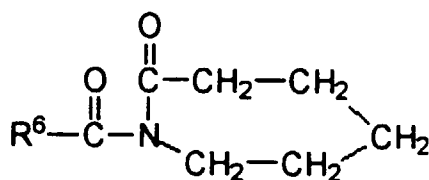
4. A method according to the preceding claims, wherein said bleach activator is selected from the group consisting of:

a) a bleach activator of the formula:



or mixtures thereof, wherein R¹ is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R² is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R⁵ is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is leaving group;

b) a N-acyl caprolactam bleach activator of the formula:



wherein R⁶ is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons; and

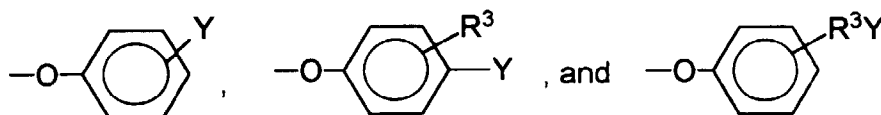
c) mixtures of a) and b);

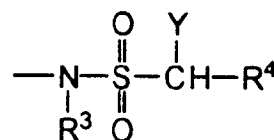
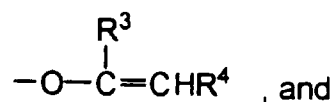
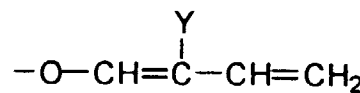
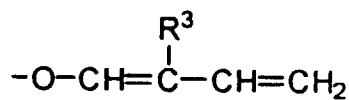
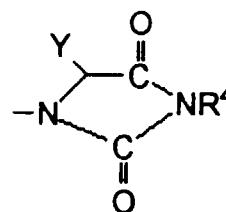
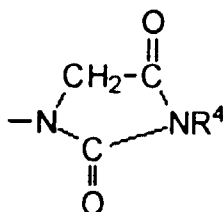
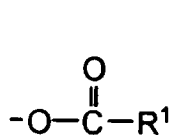
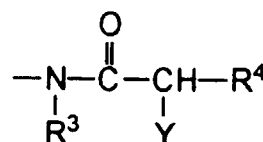
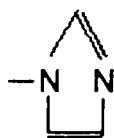
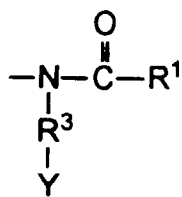
and said enzyme is selected from the group consisting of SAVINASE, Protease C, and mixtures thereof.

5. A method according to the preceding claims, wherein said bleach activator is selected from the group consisting of benzoyl caprolactam, nonanoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, (6-octanamidocaproyl)oxybenzenesulfonate, (6nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof; said enzyme is Protease C; and said peroxygen bleaching compound is selected from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium percarbonate, sodium peroxide and mixtures thereof.

6. A method according to the preceding claims wherein the molar ratio of hydrogen peroxide to bleach activator is greater than 1.0.

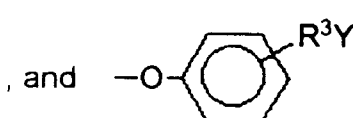
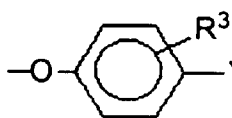
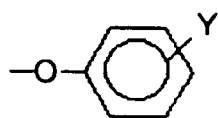
7. A method according to claims 1 to 4, wherein R¹ is an alkyl group containing from 6 to 12, preferably from 7 to 10, carbon atoms; R² contains from 1 to 8, preferably from 4 to 5, carbon atoms; R⁵ is H or methyl; and L is selected from the group consisting of:





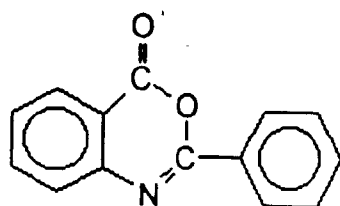
and mixtures thereof; wherein R^1 is as defined in Claim 1, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group.

8. A method according to Claim 7 wherein L is selected from the group consisting of:



wherein R^3 is an alkyl chain containing from 1 to 8 carbon atoms, Y is $-\text{SO}_3^-\text{M}^+$ or $-\text{CO}_2^-\text{M}^+$ wherein M is sodium or potassium.

9. A composition according to Claim 1 wherein said benzoxazin-type bleach activator has the formula:



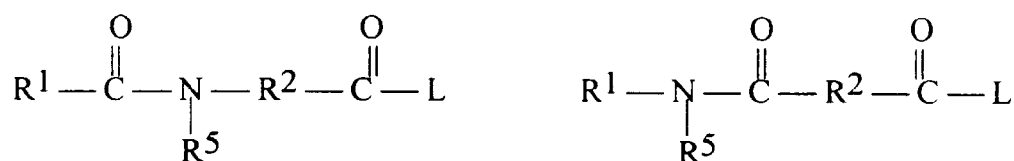
10. A method according to the preceding claims, where said composition further comprises from 5% to 80%, by weight,

of a deterative surfactant; from 5% to 80%, by weight, of a deterative builder; and from 0% to 20%, by weight, of conventional deterative adjuncts.

Revendications

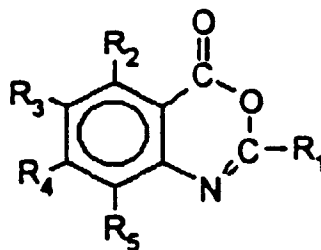
- Procédé pour nettoyer du linge dans une machine à laver automatique possédant des pièces en caoutchouc naturel, lequel est susceptible de subir une détérioration par oxydation, ledit procédé comprenant le fait d'agiter ledit linge dans ladite machine dans une liqueur aqueuse comprenant une composition détergente contenant une quantité efficace d'un ou de plusieurs types d'enzymes et un système de blanchiment comprenant au moins 0,1% en poids d'un composé de blanchiment peroxygéné capable de produire du peroxyde d'hydrogène dans une liqueur aqueuse et au moins 0,1% en poids d'un ou de plusieurs activateurs de blanchiment, dans lequel lesdits activateurs de blanchiment sont choisis dans le groupe constitué par:

a) un activateur de blanchiment de formule générale:



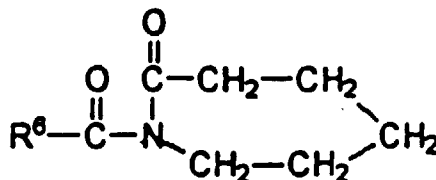
ou leurs mélanges, formules dans lesquelles R¹ est un groupe alkyle, aryle ou alkaryle contenant de 1 à 14 atomes de carbone, R² est un groupe alkylène, arylène ou alkarylène contenant de 1 à 14 atomes de carbone, R⁵ est H ou un groupe alkyle, aryle ou alkaryle contenant de 1 à 10 atomes de carbone et L est un groupe partant;

b) un activateur de blanchiment de type benzoxazine de formule:



dans laquelle R₁ est H, un groupe alkyle, alkaryle, aryle, arylalkyle, et dans laquelle R₂, R₃, R₄ et R₅ peuvent être des substituants identiques ou différents choisis parmi H, un halogène, un groupe alkyle, alcényle, aryle, hydroxyle, alcoxyle, amino, alkylamino, -COOR₆, où R₆ est H ou un groupe alkyle, et des fonctions carbonyle;

c) un activateur de blanchiment de type N-acylcaprolactame de formule:

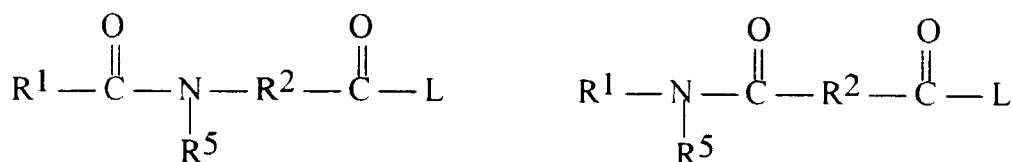


dans laquelle R⁶ est H ou un groupe alkyle, aryle, alcoxyaryle ou alkaryle contenant de 1 à 12 atomes de carbone; et d) des mélanges de a), b) et c).

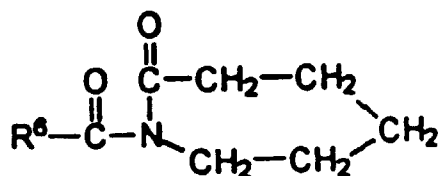
- Procédé selon la revendication 1, caractérisé en ce que lesdits enzymes constituent au moins 0,001% en poids de ladite composition détergente et sont choisies dans le groupe constitué par les protéases, les amylases, les

3. Procédé selon la revendication 2, caractérisé en ce que ladite enzyme est une lipase dérivée du champignon Humicola lanuginosa ou une sérine protéase bactérienne modifiée dérivée de Bacillus subtilis, Bacillus lentus ou Bacillus licheniformis.

a) un activateur de blanchiment de formule:



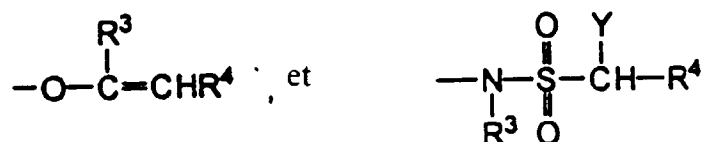
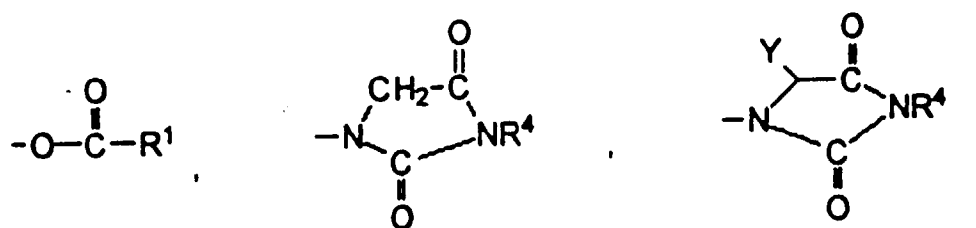
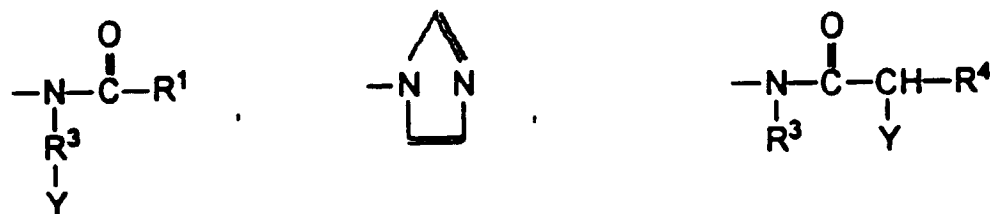
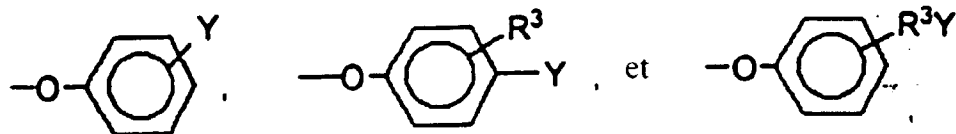
b) un activateur de blanchiment de type N-acylcaprolactame de formule:



c) des mélanges de a) et b):

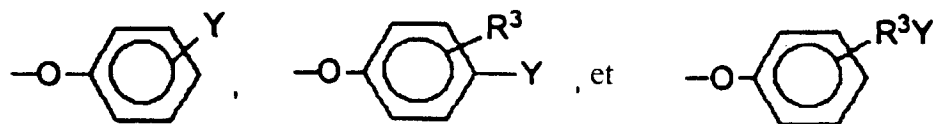
5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ledit activateur de blanchiment est choisi dans le groupe constitué par le benzoïlcaprolactame, le nonanoïlcaprolactame, l'octanoïlcaprolactame, le 3,5,5-triméthylhexanoïlcaprolactame, le décanoïlcaprolactame, l'undécénoïlcaprolactame, l'oxybenzènesulfonate de 6-octanamidocaproyle, l'oxybenzènesulfonate de 6-nonanamidocaproyle, l'oxybenzènesulfonate de 6-décanamidocaproyle, et leurs mélanges ; ladite enzyme est la Protéase C ; et ledit composé de blanchiment peroxygéné est choisi dans le groupe constitué par le perborate de sodium monohydraté, le perborate de sodium tétrahydraté, le pyrophosphate de sodium peroxyhydraté, l'urée peroxyhydratée, le percarbonate de sodium, le peroxyde de sodium, et leurs mélanges.

7. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel R^1 est un groupe alkyle contenant de 6 à 12, de préférence de 7 à 10, atomes de carbone; R^2 contient de 1 à 8, de préférence de 4 à 5, atomes de carbone; R^5 est H ou un groupe méthyle; et L est choisi dans le groupe constitué par:



40 et leurs mélanges, formules dans lesquelles R¹ est tel que défini dans la revendication 1, R³ est une chaîne alkyle contenant de 1 à 8 atomes de carbone, R⁴ est H ou R³, et Y est H ou un groupe solubilisant.

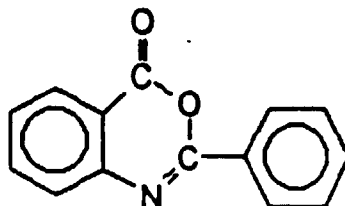
8. Procédé selon la revendication 7, caractérisé en ce que L est choisi dans le groupe constitué par:



formules dans lesquelles R³ est une chaîne alkyle contenant de 1 à 8 atomes de carbone, Y est -SO₃⁻M⁺ ou -CO₂⁻M⁺, où M est un sodium ou un potassium.

9. Procédé selon la revendication 1, caractérisé en ce que ledit activateur de blanchiment de type benzoxazine répond à la formule:

55

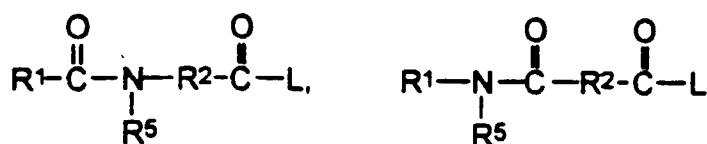


10. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ladite composition comprend, en outre, de 5% à 80%, en poids, d'un tensioactif détersif, de 5% à 80%, en poids, d'un adjuvant détersif, et de 0% à 20%, en poids, d'additifs détersifs classiques.

Patentansprüche

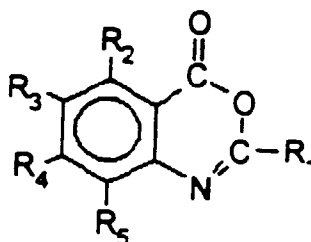
1. Verfahren zum Reinigen von Textilien in einer automatischen Waschmaschine, welche Teile aufweist, die aus natürlichem Kautschuk hergestellt sind, welcher gegenüber oxidativem Abbau anfällig ist, wobei das Verfahren das Bewegen der Textilien in der Maschine in einer wäßrigen Flotte umfaßt, welche eine Waschmittelzusammensetzung enthält, umfassend eine wirksame Menge eines oder mehrerer Typen von Enzymen und ein Bleichmittelsystem, umfassend mindestens 0,1 Gew.-% einer Persauerstoff-Bleichmittelverbindung, die in der Lage ist, Wasserstoffperoxid in einer wäßrigen Flotte zu erzielen und mindestens 0,1 Gew.-% eines oder mehrerer Bleichaktivatoren, wobei die Bleichaktivatoren Vertreter sind, gewählt aus der Gruppe, bestehend aus:

a) einem Bleichaktivator der allgemeinen Formel:



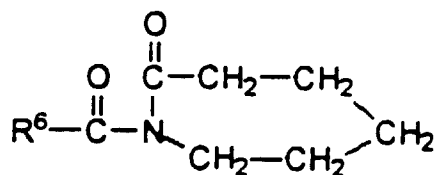
oder Mischungen hiervon, worin R¹ eine Alkyl-, Aryl- oder Alkarylgruppe mit 1 bis 14 Kohlenstoffatomen ist, R² eine Alkyl-, Aryl- oder Alkarylgruppe mit 1 bis 14 Kohlenstoffatomen ist, R⁵ H oder eine Alkyl-, Aryl- oder Alkarylgruppe mit 1 bis 10 Kohlenstoffatomen ist, und L eine Abgangsgruppe ist;

b) einem Bleichaktivator vom Benzoxazin-Typ der Formel:



worin R₁ H, Alkyl, Alkaryl, Aryl, Arylalkyl ist und worin R₂, R₃, R₄ und R₅ gleiche oder verschiedene Substituenten sein können, gewählt aus H, Halogen, Alkyl, Alkenyl, Aryl, Hydroxyl, Alkoxy, Amino, Alkylamino, -COOR₆, worin R₆ H oder eine Alkylgruppe ist, und Carbonylfunktionen;

c) einem N-Acylcaprolactam-Bleichaktivator der Formel:

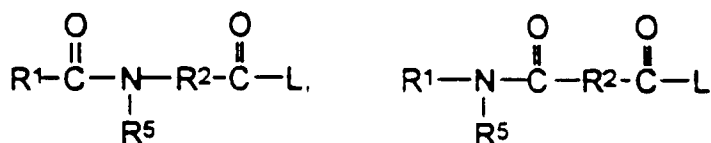


worin R_6 H oder eine Alkyl-, Aryl-, Alkoxyaryl- oder Alkarylgruppe mit 1 bis 12 Kohlenstoffatomen ist; und

d) Mischungen von a), b) und c).

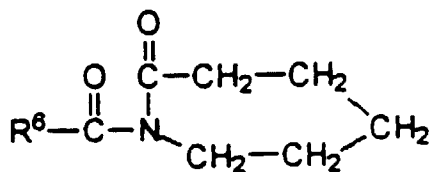
2. Verfahren nach Anspruch 1, wobei die Enzyme mindestens 0,001 Gew.-% der Waschmittelzusammensetzung umfassen und aus der Gruppe gewählt sind, bestehend aus Proteasen, Amylasen, Lipasen, Cellulasen, Peroxidasen und Mischungen hiervon.
3. Verfahren nach Anspruch 2, wobei das Enzym Lipase ist, abgeleitet von dem Pilz *Humicola lanuginosa* oder eine modifizierte bakterielle Serinprotease, abgeleitet von *Bacillus subtilis*, *Bacillus lentus* oder *Bacillus licheniformis*.
4. Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei der Bleichaktivator aus der Gruppe gewählt ist, bestehend aus:

a) einem Bleichaktivator der Formel:



oder Mischungen hiervon, worin R^1 eine Alkyl-, Aryl- oder Alkarylgruppe mit 1 bis 14 Kohlenstoffatomen ist, R^2 eine Alkyl-, Aryl- oder Alkarylgruppe mit 1 bis 14 Kohlenstoffatomen ist, R^5 H oder eine Alkyl-, Aryl- oder Alkarylgruppe mit 1 bis 10 Kohlenstoffatomen ist, und L eine Abgangsgruppe ist;

b) einem N-Acylcaprolactam-Bleichaktivator der Formel:



worin R_6 H oder eine Alkyl-, Aryl-, Alkoxyaryl- oder Alkarylgruppe mit 1 bis 12 Kohlenstoffatomen ist; und

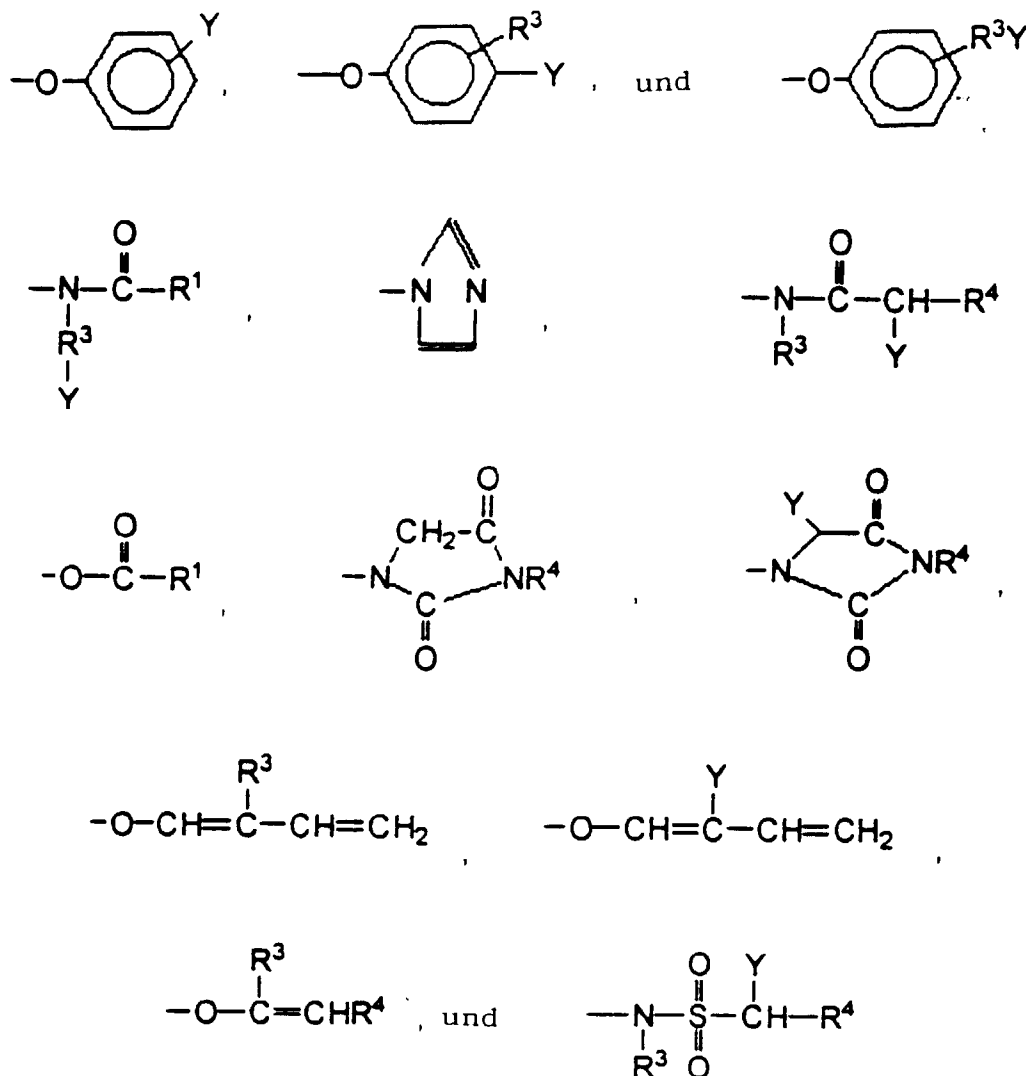
c) Mischungen von a) und b);

und wobei das Enzym aus der SAVINASE, Protease C und Mischungen hiervon umfassenden Gruppe gewählt ist.

5. Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei der Bleichaktivator aus der Gruppe gewählt ist, bestehend aus Benzoylcaprolactam, Nonacylcaprolactam, Octanoylcaprolactam, 3,5,5-Trimethylhexanoylcaprolactam, Decanoylcaprolactam, Undecenoylcaprolactam, (6-Octanamidocaproyl)oxybenzolsulfonat, (6-Nonanamidocaproyl)oxybenzolsulfonat, (6-Decanamidocaproyl)oxybenzolsulfonat und Mischungen hiervon;

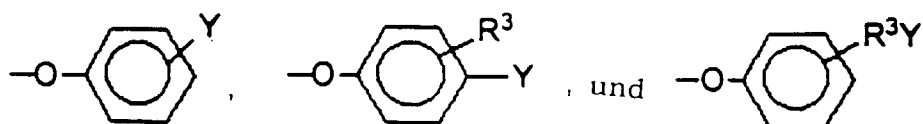
das Enzym Protease C ist; und die Persauerstoff-Bleichmittelverbindung aus der Gruppe gewählt ist, bestehend aus Natriumperboratmonohydrat, Natriumperborattetrahydrat, Natriumpyrophosphatperoxyhydrat, Harstoffperoxyhydrat, Natriumpercarbonat, Natriumperoxid und Mischungen hiervon.

6. Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei das Molverhältnis von Wasserstoffperoxid zu Bleichaktivator größer als 1,0 ist.
7. Verfahren nach den Ansprüchen 1 bis 4, wobei R¹ eine Alkylgruppe mit 6 bis 12, vorzugsweise 7 bis 10 Kohlenstoffatomen ist; R² 1 bis 8, vorzugsweise 4 bis 5 Kohlenstoffatome enthält; R⁵ H oder Methyl ist; und L aus der Gruppe gewählt ist, bestehend aus:



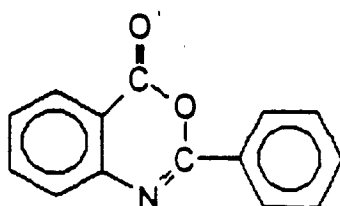
und Mischungen hiervon, worin R¹ wie in Anspruch 1 definiert ist, R³ eine Alkylkette mit 1 bis 8 Kohlenstoffatomen ist, R⁴ H oder R³ ist, und Y H oder eine solubilisierende Gruppe ist.

8. Verfahren nach Anspruch 7, wobei L aus der Gruppe gewählt ist, bestehend aus:



worin R^3 eine Alkylkette mit 1 bis 8 Kohlenstoffatomen ist, Y $-SO_3^-M^+$ oder $CO_2^-M^+$ ist, worin M Natrium oder Kalium ist.

9. Zusammensetzung nach Anspruch 1, wobei der Bleichaktivator vom Benzoxazin-Typ der Formel entspricht:



- 25 10. Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei die Zusammensetzung weiterhin 5 bis 80 Gew.-% eines Waschtensids; 5 bis 80 Gew.-% eines Waschmittelbuilders; und 0 bis 20 Gew.-% herkömmliche Waschmittelzusatzstoffe umfaßt.