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(54) Title: BLEACHING COMPOSITIONS COMPRISING PEROXYACID ACTIVATORS HAVING AMIDE MOIETIES		
(57) Abstract The present invention relates to a method of cleaning fabrics in washing machines which have parts made of natural rubber using laundry detergents comprising amido-derived bleaching activators and a source of hydrogen peroxide such that said natural rubber parts of said machines are substantially undamaged by products of the perhydrolysis reaction between the activator and hydrogen peroxide.		

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BLEACHING COMPOSITIONS COMPRISING
PEROXYACID ACTIVATORS HAVING AMIDE MOIETIES

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FIELD OF THE INVENTION

The present invention relates to laundry detergents with activated bleaching systems.

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BACKGROUND OF THE INVENTION

It has 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 wash liquor temperature of 60°C, peroxygen bleaches are only partially effective. As the wash 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 wash liquor temperatures below 60°C.

Numerous substances have been disclosed in the art as effective bleach activators. One widely-used bleach 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. Another type of activator, such as nonanoyl-oxybenzenesulfonate (NOBS) and other activators which generally comprise long chain alkyl moieties, is hydrophobic in nature and provides excellent performance on dingy stains. However, many of the hydrophobic activators developed thus far can promote damage to natural rubber parts used in certain washing machines. Because of these negative effects on washing machine parts, the selection of such detergent-added bleaching systems has long been limited. This is especially true for European detergent/bleaches, since many washing machines manufactured in Europe have been equipped with key parts, such as sump hoses and motor gaskets, made of natural rubber. A need, therefore, exists for a bleaching system which provides dingy soil clean up

without substantially damaging the natural rubber parts found in washing machines.

It has now been determined that in conventional bleaching systems, typically comprising a hydrophobic bleach activator and a source of hydrogen peroxide, the activator undergoes perhydrolysis to form a peroxyacid bleaching agent. A by-product of the perhydrolysis reaction between such bleach activators and hydrogen peroxide is a diacylperoxide (DAP) species. It has now further been discovered that the DAP's derived from hydrophobic bleaching 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 wash liquor. The oily DAP residue can form a film on the natural rubber parts and promote free radical and peroxide damage to the rubber, which eventually leads to failure of the parts. This is particularly true of rubber parts which have prolonged exposure to the wash liquor, such as sump hoses.

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. Without limiting the invention herein, it is believed that the DAP's produced by the perhydrolysis reaction of the amido acid-derived bleach activators are insoluble crystalline solids. Such solid DAP's do not form a coating film. Accordingly, the natural rubber machine parts are not exposed to the DAP's for extended periods of time and remain substantially undamaged by the bleaching system of the present invention.

The present invention thus solves the long-standing need for an effective hydrophobic bleaching system which does not promote free radical and peroxide damage to natural rubber parts in washing machines. The invention provides a method of cleaning fabrics with a bleaching system in washing machines which have parts made of natural rubber such that the natural rubber is substantially undamaged by the bleaching system.

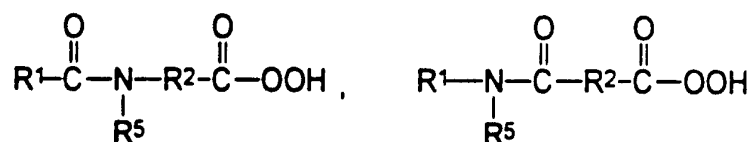
BACKGROUND ART

U.S. Patent 4,634,551, Burns et al, issued January 6, 1987, discloses amido peroxyacid bleaching compounds and their precursors of the type employed in the present invention. See also, U.S. Patent 4,852,989, Burns et al, issued August 1, 1989, and U.S. Patent 4,966,723, Hodge et al, issued Oct. 30, 1990.

SUMMARY OF THE INVENTION

The present invention relates to a method for cleaning fabrics in automatic washing machines having parts made of natural rubber which is susceptible to oxidative degradation. The method comprises agitating fabrics in said washing machine in an aqueous liquor comprising a bleaching system comprising a bleach activator which reacts with a source of peroxide in said aqueous liquor to yield a peroxyacid without the formation of oily diacylperoxide (DAP) such that said natural rubber parts are substantially undamaged by the by-products of said reaction.

The amido-derived peroxyacids generated by the reaction are of the general formulas:



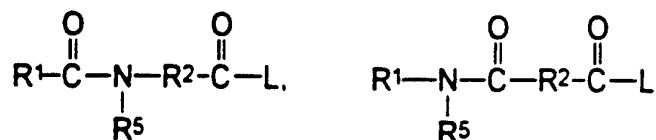
wherein R^1 is an alkyl, aryl, or alkaryl group containing from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene or alkarylene group containing from about 1 to about 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing from about 1 to about 10 carbon atoms.

The bleaching system of said method comprises:

a) at least about 0.1%, preferably from about 1% to about 75%, by weight, of a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous liquor; and

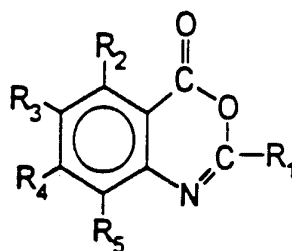
b) at least about 0.1%, preferably from about 0.1% to about 50%, by weight, of a bleach activator selected from the group consisting of:

i)



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

ii)



wherein R_1 is H, alkyl, alkaryl, aryl, aralkyl, 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, alkoxyl, amino, alkylamino, COOR_6 (wherein R_6 is H or an alkyl group) and carbonyl functions; and

iii) mixtures of i) and ii).

Preferably the molar ratio of hydrogen peroxide yielded by a) to bleach activator b) is greater than about 1.0. Most preferably, the molar ratio of hydrogen peroxide yielded by a) to bleach activator b) is at least about 1.5.

The invention also encompasses laundry compositions in granular, paste, liquid, or bar form which comprise the aforesaid bleaching system together with detergent ingredients which are present in the composition at the levels indicated hereinafter.

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

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

The peroxygen bleaching compound can be any peroxide source and is preferably a member selected from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate, sodium percarbonate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide and mixtures thereof. Highly preferred peroxygen bleaching compounds are selected from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate, sodium percarbonate and mixtures thereof. The most highly preferred peroxygen bleaching compound is sodium percarbonate.

The bleach activators herein can also be used in combination with rubber-safe, hydrophilic activators such as TAED, typically at weight ratios of amido-derived activators:TAED in the range of 1:5 to 5:1, preferably about 1:1. Another important class of rubber- safe, hydrophilic activators comprise the N-acyl caprolactam activators wherein the acyl moiety has the formula R^1-CO- wherein R^1 contains 6 or less carbon atoms. Highly preferred hydrophilic caprolactam activators include formyl caprolactam, acetyl caprolactam, and benzoyl caprolactam.

The method of cleaning fabrics comprises agitating fabrics in said washing machine in an aqueous liquor comprising a detergent composition which comprises at least about 300 ppm of conventional detergent ingredients, at least about 25 ppm of the bleaching compound and at least about 25 ppm of a bleach activator. Preferably, the liquor comprises from about 900 ppm to about 20,000 ppm of conventional detergent ingredients, from about 100 ppm to about 25,000 ppm of the bleaching compound and from about 100 ppm to about 2,500 ppm of a bleach activator. The method can be successfully carried out at temperatures below about 60°C but, of course, is quite effective and is still safe to rubber parts at laundry temperatures up to the boil.

The conventional detergent ingredients employed in fully formulated detergent compositions provided herein can comprise from about 1% to about 99.8%, preferably from about 5% to about 80%, of a deterative surfactant. Optionally, detergent compositions can comprise from about 5% to about 80% of a deterative builder. Other optional detergent ingredients are also encompassed by the fully-formulated detergent/bleach compositions provided by this invention.

All percentages, ratios, and proportions are by weight, unless otherwise specified. All documents cited are incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to a method for cleaning fabrics in automatic washing machines having parts made of natural rubber which is susceptible to oxidative degradation. The bleaching system used in this invention is safe to natural rubber machine parts and to other natural rubber articles which are exposed to the bleaching system, including fabrics containing natural rubber and natural rubber elastic materials. The bleaching system employed in the present invention provides effective and efficient surface bleaching of fabrics which thereby removes stains and/or soils, including "dingy" soils, from the

fabrics. Dingy soils are soils that build up on fabrics after numerous cycles of usage and washing and, thus, eventually cause white fabrics to have a gray or yellow tint. These soils tend to be a blend of particulate and greasy materials. The removal of this type of soil is sometimes referred to as "dingy fabric clean up".

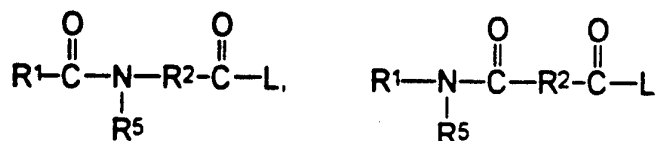
The bleaching systems and activators herein afford additional advantages in that, unexpectedly, they are safer to fabrics and cause less color damage than other activators when used in the manner provided by this invention.

The bleaching mechanism and, in particular, the surface bleaching mechanism are not completely understood. However, it is generally believed that the bleach activator undergoes nucleophilic attack by a perhydroxide anion, which is generated from the hydrogen peroxide evolved by the peroxygen bleach, to form a peroxycarboxylic acid. This reaction is commonly referred to as perhydrolysis.

It is also believed, that the bleach activators within the invention can render peroxygen bleaches more efficient even at wash 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 Bleach Activator

The hydrophobic bleach activators employed with this invention are amide substituted compounds of the general formulas:

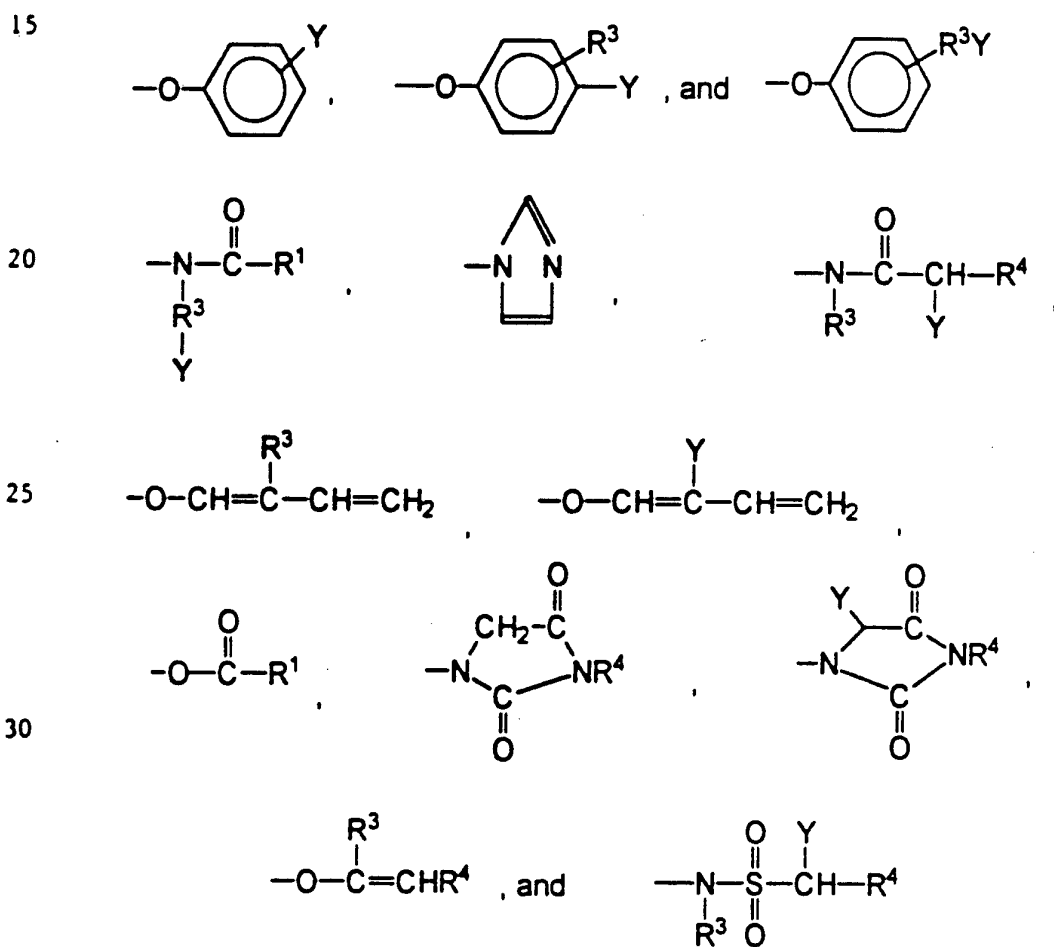


or mixtures thereof, wherein R¹, R², and R⁵ are as defined hereinabove and L can be essentially any suitable leaving group. A leaving group is any group that is displaced from the bleaching activator as a consequence of the nucleophilic attack on the bleach activator by the perhydroxide anion. This, 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 about 4 to about 13, preferably from about 6 to about 11 and most preferably from about 8 to about 11.

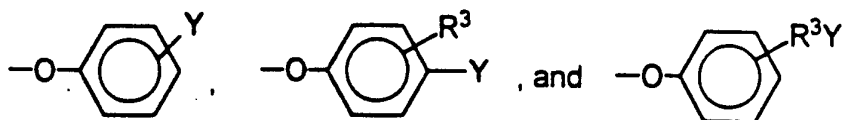
Preferred bleach activators are those of the above general formula wherein R^1 , R^2 and R^5 are as defined for the peroxyacid and L is selected from the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from about 1 to about 14 carbon atoms, R^3 is an alkyl chain containing from 1 to about 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 about 1 to about 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.

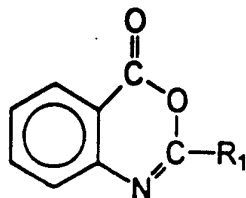
Preferred bleach activators are those of the above general formula wherein L is selected from the group consisting of:



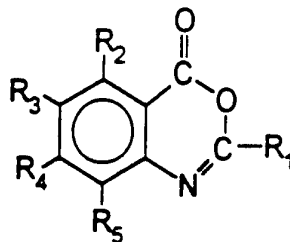
wherein R^3 is as defined above and Y is $-\text{SO}_3^- \text{M}^+$ or $-\text{CO}_2^- \text{M}^+$ wherein M is as defined above.

Another important class of bleach activators which provide organic peracids as described herein ring-opens as a consequence of the nucleophilic attack on the carbonyl carbon of the cyclic ring by the perhydroxide anion. This ring-opening reaction involves attack at the ring carbonyl by hydrogen peroxide or its anion. Examples of ring-opening bleach activators can be found 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:

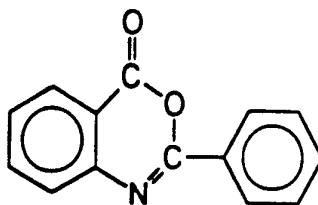


including the substituted benzoxazins of the type



wherein R_1 is H, alkyl, alkaryl, aryl, aralkyl, 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:



The bleach activators employed herein will comprise at least about 0.1%, preferably from about 0.1% to about 50%, more preferably from about 1% to about 30%, most preferably from about 3% to about 25%, by weight of the 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 about 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 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 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 percarbonate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Particularly preferred are sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate. Sodium 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 about 400 to about 1200 microns, most preferably from about 400 to about 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 about 0.1%, preferably from about 1% to about 75%, more preferably from about 3% to about 40%, most preferably from about 3% to about 25%, by weight of the bleaching system or detergent composition.

The weight ratio of bleach activator to peroxygen bleaching compound in the bleaching system ranges from about 2:1 to about 1:5. In preferred embodiments, the ratio ranges from about 1:1 to about 1:3.

The bleach activator/bleaching compound systems herein are useful per se as bleaches. However, such bleaching systems are especially useful in compositions which can comprise various detergent adjuncts such as surfactants, builders, enzymes, and the like as disclosed hereinafter.

Detergent Surfactant

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

The detergent surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used.

Preferred detergent compositions comprise anionic deterative 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 ethoxylates 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 ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl 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

alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R^1 is preferably methyl or hydroxyalkyl. If lower sudsing is desired, R^1 is preferably $\text{C}_2\text{-C}_8$ alkyl, especially n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

$\text{R}^2\text{-CO-N}\leftarrow$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

10 Detergent Builders

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

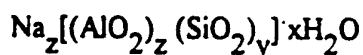
15 Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates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

20 Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2\text{:Na}_2\text{O}$ 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.

25 Carbonate builders, especially a finely ground calcium carbonate with surface area greater than $10 \text{ m}^2/\text{g}$, 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%.

30 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.

35 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 about 0.5, and x is an integer from about 15 to about 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 deterative 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.

Other useful deterative builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic 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-laundering 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.

5 Optional Deterasive Adjuncts

As a preferred embodiment, the conventional detergent ingredients employed herein can be selected from typical detergent composition components such as deterative surfactants and deterative builders. Optionally, the detergent ingredients can include one or more other deterative 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 deterative adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. Adjuncts which can also be included in detergent compositions employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 20% of the detergent ingredients, preferably from about 0.5% to about 10%), include enzymes, especially proteases, lipases, and cellulases, 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, enzyme stabilizing agents, perfumes, solvents, solubilizing agents, clay soil removal/anti-redeposition agents, polymeric dispersing agents, processing aids, fabric softening components, static control agents, etc.

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 amino-phosphonates, 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 ethylenediamine 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 about 0.1% to about 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.

Specific examples of optional bleach activators for incorporation in this invention include tetraacetyl ethylene diamine (TAED) and N-acyl caprolactams. Highly preferred N-acyl caprolactams include benzoyl caprolactam and those wherein the acyl moieties have the formula R^1 -CO- wherein R^1 is H or an alkyl, aryl, alkaryl, or alkoxyaryl group containing from 1 to 12 carbon atoms, preferably 1 to 6 carbon atoms.

Such bleaching compounds and agents can be optionally included in detergent compositions in their conventional art-established levels of use, generally from 0% to about 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 (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

16

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) 476 g (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 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 II

A granular detergent compositions is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
35	C ₁₂ linear alkyl benzene sulfonate	22
	Phosphate (as sodium tripolyphosphate)	30

	Sodium carbonate	14
	Sodium silicate	3
	Sodium percarbonate	5
	Ethylenediamine disuccinate chelant (EDDS)	0.4
5	Sodium sulfate	5.5
	(6-Nonanamidocaproyl)oxybenzenesulfonate	5
	Minors, filler* and water	Balance to 100%

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

10 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. The other ingredients are admixed so that the composition contains the ingredients tabulated at the
15 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 fabrics, to an automatic washing machine equipped with a natural rubber sump hose. Actual weights of detergent and bleach activator are
20 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 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
25 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 damage to the natural rubber articles.

EXAMPLE III

A granular detergent composition is prepared comprising the following
30 ingredients.

	<u>Component</u>	<u>Weight %</u>
	Anionic alkyl sulfate	7
	Nonionic surfactant	5
	Zeolite (0.1-10 micron)	10
35	Trisodium citrate	2
	SKS-6 silicate builder	10

	Acrylate maleate polymer	4
	(6-Nonanamidocaproyl)oxybenzenesulfonate	5
	Sodium percarbonate	15
	Sodium carbonate	5
5	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Suds suppressor	2
	Enzymes*	1.5
	Soil release agent	0.2
	Minors, filler** and water	Balance to 100%
10	*1:1:1 mixture of protease, lipase, and cellulase.	
	**Can be selected from convenient materials such as CaCO_3 , 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:

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

20 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 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 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.

30 EXAMPLE IV

A detergent composition is prepared by a procedure identical to that of Example III, with the single exception that an equivalent amount of nonanoyloxybenzenesulfonate (NOBS) is substituted for the (6-Nonanamidocaproyl)oxybenzenesulfonate bleach activator in Example III. The laundering method of Example III is repeated for 1200 cycles at about which time the natural rubber sump hose ruptures.

EXAMPLE V

A detergent composition is prepared by a procedure identical to that of Example III, with the single exception that an equivalent amount of benzyloxybenzenesulfonate (BOBS) is substituted for the (6-Nonanamido-
5 caproyl)oxybenzenesulfonate bleach activator in Example III. The laundering method of Example III is repeated for 1200 cycles at about which time the natural rubber sump hose ruptures.

EXAMPLE VI

A detergent composition is prepared by a procedure identical to that of
10 Example III, with the exceptions that 15% of a 1:1 mixture of tetraacetyl ethylene diamine and (6-Nonanamidocaproyl)oxybenzenesulfonate bleach activator is substituted for the bleach activator in Example III and the amount of sodium percarbonate is 30%. The laundering method of Example III is repeated for 2,000 cycles without rupture of, or significant damage to, the
15 natural rubber parts.

EXAMPLE VII

A detergent composition is prepared by a procedure identical to that of Example III, with the single exception that 15% of a 1:1 mixture of benzoyl caprolactam and (6-Nonanamidocaproyl)oxybenzenesulfonate is substituted for
20 the bleach activator in Example III and the amount of sodium percarbonate is 30%. The laundering method of Example III is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts.

EXAMPLE VIII

A detergent composition is prepared by a procedure identical to that of
25 Example III, with an equivalent amount of a benzoxazin-type bleaching activator, as disclosed in U.S. Patent 4,966,723, Hodge et al, is substituted for the bleach activator in Example III. The laundering method of Example III is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts.

EXAMPLE IX

A detergent composition is prepared by a procedure identical to that of Example III, with the single exception that 6% of a 1:1 mixture of (6-Nonanamidocaproyl)oxybenzenesulfonate and a benzoxazin-type bleaching activator, as disclosed in U.S. Patent 4,966,723, Hodge et al, is substituted for the bleach
35 activator in Example III. The laundering method of Example III is repeated for

2,000 cycles without rupture of, or significant damage to, the natural rubber parts.

EXAMPLE X

A detergent composition is prepared by a procedure identical to that of Example III, with the single exception that 6% of a 1:1 mixture of tetraacetyl ethylene diamine and a benzoxazin-type bleaching activator, as disclosed in U.S. Patent 4,966,723, Hodge et al, is substituted for the bleach activator in Example III. The laundering method of Example III is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts.

Method of Processing the Bleach Activators

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.

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

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.

A typical particle composition is about 40% to about 60%, preferably about 55%, by weight, of the bleach activator or mixture of bleach activators; about 20% to about 40%, preferably about 25%, by weight, of citric acid; and about 15% to about 30%, preferably about 20%, by weight of TAE25 binding agent. Alternatively, a 2:1 mixture of (6-decanamidocaproyl)oxyben-

zenesulfonate 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.

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

EXAMPLE XI

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

<u>Component</u>	<u>Weight %</u>
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
Ethylenediamine disuccinate chelant (EDDS)	0.4
Polyacrylate (m.w. 1400)	0.2
(6-Nonanamidocaproyl)oxybenzenesulfonate	5
Sodium percarbonate*	5
Brightener, perfume	0.2
Protease	0.3
CaSO ₄	1
MgSO ₄	1
Water	4
Filler**	Balance to 100%

*Average particle size of 400 to 1200 microns.

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

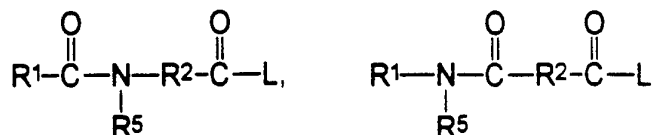
5 The detergent laundry bars are processed in conventional soap or detergent bar making equipment as commonly used in the art. Testing is conducted following the testing methods in Example II. The laundering method is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts, or damage to the natural rubber articles.

What is claimed is:

1. A bleaching system characterized in that it comprises:

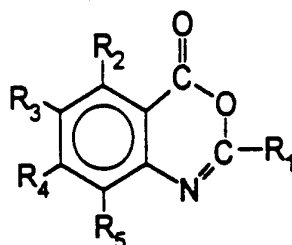
a) a bleach activator selected from the following:

i)



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; and

ii)

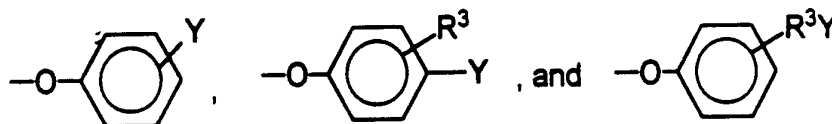


wherein R_1 is H, alkyl, alkaryl, aryl, aralkyl, and wherein R_2 , R_3 , R_4 , and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxyl, amino, alkylamino, $-\text{COOR}_6$, wherein R_6 is H or an alkyl group and carbonyl functions;

b) a nonamido-derived hydrophilic bleach activator; and

c) a peroxygen bleaching compound, preferably selected from the group consisting of perborate salts and percarbonate salts..

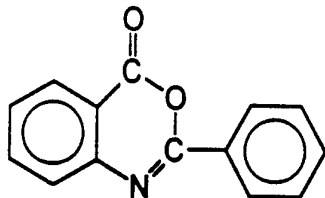
2. A composition according to Claim 1 wherein R^1 is an alkyl group containing from 7 to 10 carbon atoms, R^2 contains from 4 to 5 carbon atoms, and L is selected from the group consisting of:



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.

3. A composition according to Claim 1 wherein the hydrophilic bleach activator is selected from the group consisting of benzoyl caprolactam and tetraacetyl ethylene diamine.

4. A composition according to Claim 1 wherein the bleach activator is

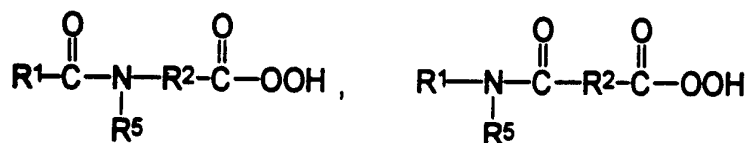


5. A composition according to Claim 1 which additionally comprises a chelant, preferably an ethylenediamine disuccinate chelant or an aminophosphonate chelant.

6. A composition according to Claim 1 in the form of a laundry detergent which additionally comprises deterative surfactants, builders and deterative adjunct ingredients.

7. 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 bleaching system according to Claim 1, such that said natural rubber parts of said machine are substantially undamaged by the bleaching system.

8. A method according to Claim 7 wherein the bleaching system comprises a bleach activator which reacts in said aqueous liquor to yield a peroxyacid of the general formulae:



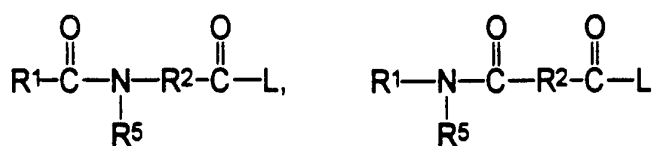
wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^2 is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms.

9. A method according to Claim 7 wherein said aqueous liquor further comprises conventional detergent ingredients; said bleaching system comprising:

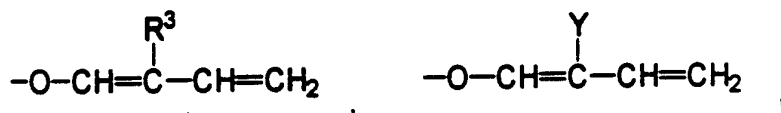
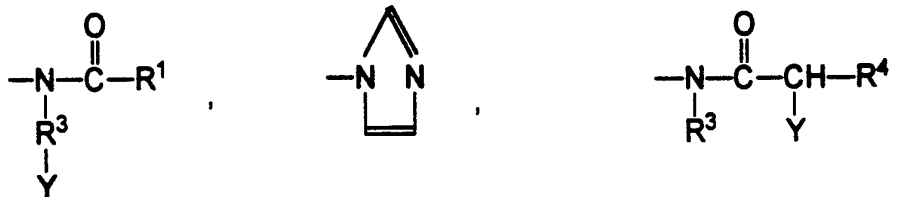
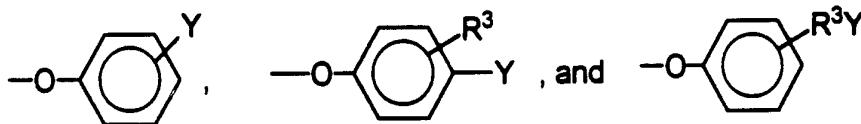
a) at least 0.1%, by weight, of a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous liquor; said peroxygen bleaching compound is preferably selected from the group consisting of sodium perborate monohydrate, sodium percarbonate, sodium perborate tetrahydrate, sodium pyrophosphate peroxy-hydrate, urea peroxyhydrate, sodium peroxide and mixtures thereof; and

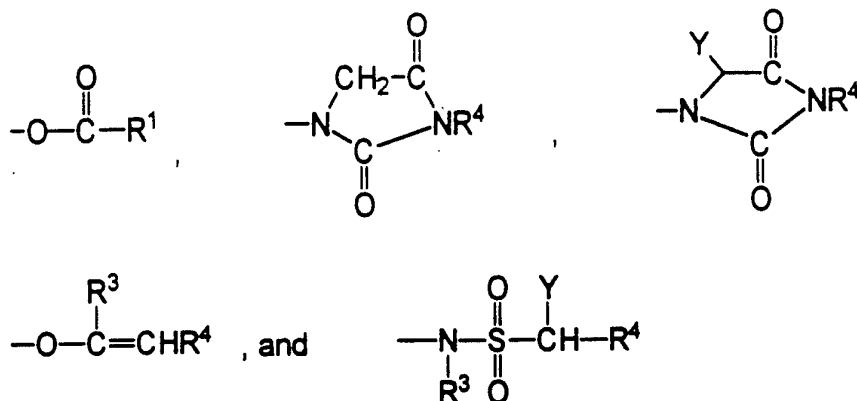
b) at least 0.1%, by weight, of a bleach activator selected from the group consisting of:

i)



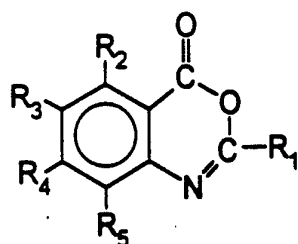
or mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^2 is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R^5 is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is a leaving group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





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; and

ii)

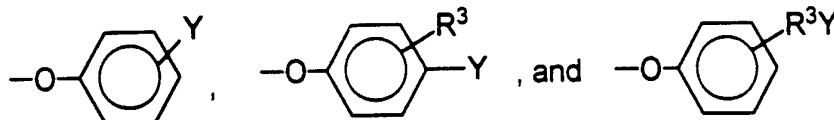


wherein R_1 is H, alkyl, alkaryl, aryl, aralkyl, and wherein R_2 , R_3 , R_4 , and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkylamino, $-\text{COOR}_6$, wherein R_6 is H or an alkyl group, and carbonyl functions, such that the molar ratio of hydrogen peroxide yielded by a) to bleach activator b) is greater than 1.0.

10. A method according to Claim 9 wherein R^1 is an alkyl group containing from 6 to 12, preferably from 7 to 10, carbon atoms, R^2 contains from 1 to 8, preferably from 4 to 5, carbon atoms, and R^5 is H or methyl.

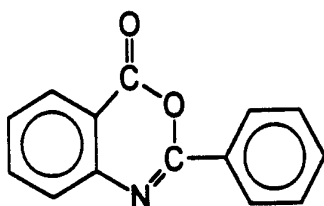
11. A method according to Claim 10 wherein Y is selected from the group consisting of: $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $-\text{N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}^-\text{N}(\text{R}^3)_3$ and mixtures thereof wherein R^3 is an alkyl chain containing 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.

12. A method according to Claim 11 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.

13. A method according to Claim 9 wherein the bleach activator is



14. A method according to Claim 9 wherein the conventional detergent ingredients comprise 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 adjunct materials.

15. A composition according to Claim 1 wherein said bleach activators are in particulate form.

16. A composition according to Claim 16 wherein said bleach activator particle comprises from 40% to 60%, by weight, of a 1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate and (6-decanamidocaproyl)oxybenzenesulfonate; from 20% to 40%, by weight, citric acid; and from 15% to 30%, by weight, tallow alcohol ethoxylate nonionic surfactant.

17. A composition according to Claim 16 wherein said bleach activator particle comprises 65% benzoyl caprolactam, 7% aluminium silicate, 15% sodium carbonate, 9% polyacrylate polymer, and 4% linear alkyl sulfonate.

18. A composition according to Claim 16 wherein said particle comprises 80% benzoyl caprolactam and 20% tallow alcohol ethoxylate nonionic surfactant.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/05370

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 332 294 (BP CHEMICALS) 13 September 1989 cited in the application see claims 1,2; examples ---	1,4,6,15
A	EP,A,0 482 806 (BP CHEMICALS) 29 April 1992 see page 3, line 21 - line 26; examples 3,4 -----	1,3,4,6,15

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 September 1994

Date of mailing of the international search report

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Information on patent family members

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