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(57) Abstract

Bleach-additives and bleaching compositions comprising particular performance boosting bleach activators are provided. More specifically, the invention relates to compositions which provide enhanced cleaning/bleaching benefits though the selection of bleach activators at mildly alkaline washing solutions or in the presence of reduced-levels of hydrogen peroxide. Included are preferred activator compounds and methods for washing fabrics, hard surfaces, and tableware using the activators.

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# BLEACHING COMPOSITIONS AND BLEACH-ADDITIVES COMPRISING BLEACH ACTIVATORS EFFECTIVE AT LOW PERHYDROXYL CONCENTRATIONS

## FIELD OF THE INVENTION

The present invention relates to improved compositions comprising bleach activators. The bleach activators enhance or boost the performance of bleaching agents such as perborate. The bleach activators are useful in fabric laundry and bleaching compositions, automatic dishwashing compositions, hard surface cleaners, bleach additives and the like.

## BACKGROUND OF THE INVENTION

The formulation of detergent compositions which effectively remove a wide variety of soils and stains from fabrics under wide-ranging usage conditions remains a considerable challenge to the laundry detergent industry. Challenges are also faced by the formulator of automatic dishwashing detergent compositions (ADD's), which are expected to efficiently cleanse and sanitize dishware, often under heavy soil loads. The problems associated with the formulation of truly effective cleaning and bleaching compositions have been exacerbated by legislation which limits the use of effective ingredients such as phosphate builders in many regions of the world.

Most conventional cleaning compositions contain mixtures of various detersive surfactants to remove a wide variety of soils and stains from surfaces. In addition, various detersive enzymes, soil suspending agents, non-phosphorus builders, optical brighteners, and the like may be added to boost overall cleaning performance. Many fully-formulated cleaning compositions contain oxygen bleach, which can be a perborate or percarbonate compound. While quite effective at high temperatures, perborates and percarbonates lose much of their bleaching function at the low to moderate temperatures increasingly favored in consumer product use. Accordingly, various bleach activators such as tetraacetylethylenediamine (TAED) and nonanoyloxybenzenesulfonate (NOBS) have been developed to potentiate the bleaching action of perborate and percarbonate across a wide temperature range. NOBS is particularly effective on "dingy" fabrics.

A limitation with activators such as the widely commercialized TAED is that the wash solution or liquor should have a pH of about 10 or higher for best results. Since soils, especially from foods, are often acidic, detergent products are frequently quite alkaline or are buffered sufficiently to maintain a high pH so the bleach activator system can operate effectively throughout the wash. However, this need runs counter to providing milder formulations which could be improved in their compatibility with fabrics, glassware and/or skin. In cleaning operations below pH 10, many of the existing bleach activators lose their effectiveness or undergo competing side reactions which produce ineffective byproducts.

The search, therefore, continues for more effective activator materials, especially for use in mildly alkaline washing liquors or with decreased levels of perborate or other sources of hydrogen peroxide. Improved activator materials should be safe, effective, and will preferably be designed to interact with troublesome soils and stains. Various activators have been described in the literature. Many are esoteric and expensive.

It has now been determined that certain selected bleach activators are unexpectedly effective in removing soils and stains from fabrics and hard surfaces such as dishes even under low alkaline wash conditions or with decreased levels of hydrogen peroxide. These activators also have advantageously high ratios of rates of perhydrolysis to hydrolysis and of perhydrolysis to diacylperoxide formation. Without being limited by theory, these unusual rate ratios lead to a number of significant benefits for the instant activators, including increased efficiency, avoidance of wasteful byproduct formation in the wash, increased color compatibility, increased enzyme compatibility, and better stability on storage.

When formulated as described herein, detergent compositions are provided using the selected bleach activators to remove soils and stains not only from fabrics, but also from dishware in automatic dishwashing compositions, from kitchen and bathroom hard surfaces, and the like, with excellent results. The activators are designed to function well over a wide range of washing or soaking temperatures and are compatible with rubber surfaces, such as those of sump hoses often used in European front-loading washing machines. In short, detergent compositions herein provide a substantial advance over those known in the art, as will be seen from the disclosures hereinafter.

## BACKGROUND ART

Bleach activators of various types are described in U.S. Patents 4,545,784; 4,013,575; 3,075,921; 3,637,339; 3,177,148; 3,042,621; 3,812,247; 3,775,332; 4,778,618; 4,790,952; EP 257,700; WO 94/18299; WO 94/18298; WO 93/20167; WO 93/12067; and in JP 02115154. Other references include Aikawa CA 85:1086z; Stehlicek CA 108:187402w; Ishida CA 88:169981y; Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 7, 4th Ed., 1993, pp. 1072-1117; Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 4, 4th Ed., 1994, pp. 271-299; Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 9, 4th Ed., 1993, pp. 567-620.

## SUMMARY OF THE INVENTION

The present invention relates to bleach-additive or bleaching compositions suitable for the domestic treatment of fabrics or hard surfaces. The compositions of this invention can further comprise a source of hydrogen peroxide, and also include embodiments which are substantially free from hydrogen peroxide or hydrogen peroxide releasing sources.

The cleaning compositions herein comprise an effective amount of one or more performance-enhanced bleach activators. These activators are selected to have particular properties so that they are more effective in promoting bleaching under certain use conditions in which TAED or similar conventional bleach activators are relatively inefficient and ineffective.

In general, suitable activators for the present cleaning compositions comprise one or more moieties RC(O)- which produce a peracid RC(O)-OOH on perhydrolysis (reaction with perhydroxyl, $^{-}OOH$). R is selected such that the difference in aqueous $pK_a$ between acetic acid and the carboxylic acid analog, RC(O)OH, of said peracid is at least 0.6, preferably at least about 1.2. When it is stated that the difference in aqueous $pK_a$ between acetic acid and the carboxylic acid analog, RC(O)OH, of a peracid is at least 0.6, the following subtraction, in the indicated order, is made: $pK_a$ ($CH_3C(O)OH$) - $pK_a$ (RC(O)OH).

These performance-enhanced bleach activators also have a low pH perhydrolysis efficiency coefficient (a practical measure of peracid formation further defined hereinafter) of greater than about 0.15, preferably greater than about 0.3, and a ratio $k_P/k_D \geq 5$, more preferably $k_P/k_D \geq 30$, still more preferably $k_P/k_D \geq 50$, wherein $k_P$ is the rate constant for perhydrolysis of the performance-enhanced bleach activator and $k_D$ is the rate constant for the formation of a diacylperoxide, RC(O)OOC(O)R, from the performance-enhanced bleach activator.

The activators herein preferably comprise one or more moieties, L, which act as leaving groups on perhydrolysis. Thus, preferred performance enhanced bleach activators herein have the formula RC(O)-L.

Preferred leaving groups, L, comprise at least one tri-coordinate nitrogen atom covalently connecting L to RC(O)-. Furthermore, the preferred performance-enhanced bleach activators are capable of forming a maximum of one mole equivalent of said peracid on perhydrolysis and have $k_H \leq 10\ M^{-1}\ s^{-1}$ and a ratio $k_P/k_H \geq 1$, more preferably $k_P/k_H \geq 2$, wherein $k_H$ is the rate constant for hydrolysis of the performance-enhanced bleach activator and $k_P$ is said rate constant for perhydrolysis.

In general, R and L can independently be neutral or can be charged either positively or negatively. In preferred compositions, both R and L are neutral wherein L is typically selected from suitably substituted or unsubstituted lactams, 2-alkyl 4,5- dihydroimidazoles, and mixtures thereof, and R is illustrated by p-nitrophenyl or, more preferably, an alkylsulfonylphenyl moiety. Suitable R moieties are illustrated at length hereinafter.

In preferred embodiments, R can be connected to -C(O)- through a carbon atom which forms part of an aromatic ring, and L can be selected such that its conjugate acid, HL, has an aqueous $pK_a$ in the range from greater than about 13 to less than about 17.

In other highly preferred embodiments, the performance-enhanced bleach activator as a whole, or simply its leaving group, L, is free from any heterocyclic moiety wherein a hydrogen atom is attached to a carbon atom that is *alpha* to both a carbonyl group and a multivalent heteroatom.

The compositions of this invention may include additional detergent additives including one or more of the following ingredients: surfactants, low-foaming automatic dishwashing surfactants, ethoxylated nonionic surfactants, bleach stable thickeners, transition-metal chelants, builders, flourescent whitening agents (also known as brighteners), and buffering agents. Compositions of this invention are typically formulated below drycleaning-useful levels of any organic solvent. Preferably the compositions are substantially free from organic solvents. Preferred builders are selected from the group consisting of citrate, layered silicate, zeolite A, zeolite P and mixtures thereof.

A typical bleach-additive composition herein comprises:

(a) from about 0.1% to about 30% of said performance-enhanced bleach activator;

(b) from about 0.1% to about 60% of nonionic surfactant; and

(c) from about 0.001% to about 10% of a transition-metal chelant.

A typical bleaching composition herein comprises:

(a) from about 0.1% to about 30% of said performance-enhanced bleach activator;

(b) from about 0.1% to about 70% of a hydrogen peroxide source; and

(c) from about 0.001% to about 10% of a transition-metal chelant.

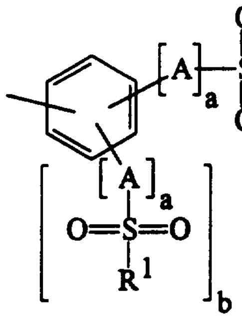
In preferred embodiments, the bleaching compositions deliver an aqueous pH in the range from about 6.5 to about 9.5, more preferably from about 7 to about 9, still more preferably from about 7.5 to about 8.5, and the level of source of hydrogen peroxide is sufficient to provide a perhydroxyl ion concentration, as measured at a pH of about 7.5, of about $10^{-4}$ to about $10^{-10}$ molar, more preferably about $10^{-5}$ to about $10^{-8}$ molar.

Additional illustrations of the bleach-additive or bleaching compositions encompassed herein are those comprising from about 0.1% to about 10% of a performance-enhanced bleach activator selected from the group consisting of: p-nitrobenzoyl caprolactam; p-nitrobenzoylvalerolactam; linear or branched $C_2$-$C_9$ alkylsulfonylbenzoylcaprolactam; linear or branched $C_2$-$C_9$ alkylsulfonylbenzoyl-valerolactam; linear or branched $C_2$-$C_9$ alkyloxysulfonylbenzoylcaprolactam; linear or branched $C_2$-$C_9$ alkyloxysulfonylbenzoylvalerolactam; linear or branched $C_2$-$C_9$ alkyl(amino)sulfonylbenzoylcaprolactam; linear or branched $C_2$-$C_9$ alkyl(amino)sul-fonylbenzoylvalerolactam; 2-furoylcaprolactam; 2-furoylvalerolactam; 3-furoylcapro-lactam; 3-furoylvalerolactam; 5-nitro-2-furoylcaprolactam; 5-nitro-2-furoylvalero-lactam; 1-naphthylcaprolactam; 1-naphthylvalerolactam; and mixtures thereof. More preferably in these embodiments, the performance-enhanced bleach activator is selected from the group consisting of linear or branched $C_2$-$C_9$ alkylsulfonyl-benzoylcaprolactam; linear or branched $C_2$-$C_9$ alkylsulfonylbenzoyl-valerolactam; linear or branched $C_2$-$C_9$ alkyloxysulfonylbenzoylcaprolactam; linear or branched $C_2$-$C_9$ alkyloxysulfonylbenzoylvalerolactam; linear or branched $C_2$-$C_9$ alkyl(amino)-sulfonylbenzoylcaprolactam; linear or branched $C_2$-$C_9$ alkyl(amino)sulfonylbenzoyl-valerolactam; 2-furoylcaprolactam; 2-furoylvalerolactam; 3-furoylcaprolactam; 3-

furoylvalerolactam; 5-nitro-2-furoylcaprolactam; 5-nitro-2-furoylvalerolactam; and mixtures thereof.

In highly preferred embodiments, these compositions further comprise a bleach catalyst at the art-disclosed levels. Such compositions have particularly significant bleaching performance enhancement as compared with otherwise identical compositions in which a conventional bleach activator such as TAED is used in place of the performance-enhanced bleach activator.

This invention also relates to novel, performance-enhanced bleach activator compounds having the formula RC(O)-L, wherein L is selected from the group consisting of lactams and 4,5-dihydroimidazoles; R is selected from the group consisting of substituted phenyl having more than one chloro, bromo or nitro substituent; furan or substituted furan having one or more chloro, bromo, nitro, alkylsulfonyl or arylalkylsulfonyl substituents; 1-naphthyl; substituted 1-naphthyl; or substituted 2-naphthyl having one or more chloro, bromo or nitro substituents;

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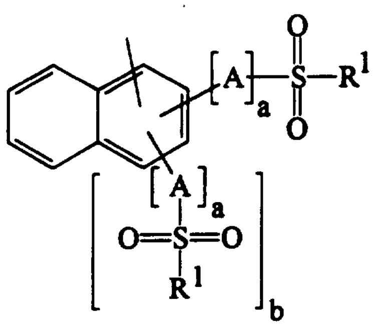



;

and mixtures thereof;

wherein in each structure a is independently 0 or 1, b is 0 or 1, and A is selected from O and $NR^2$ wherein $R^2$ is H or methyl; and wherein when a is 1 and A is O, $R^1$ is selected from alkyl, arylalkyl, alkoxy, aryloxy, alkylamino, and arylamino; when a is 1 and A is other than O, $R^1$ is selected from alkyl and arylalkyl. Compositions comprising these novel compounds are also included in the scope of this invention.

The invention also encompasses a method for removing stains from fabrics or hard surfaces, especially dishware, comprising contacting said stains with a source of hydrogen peroxide and a bleach activator compound as defined herein in the presence of water, preferably with agitation. Typically the activator will be present at levels of at least about 20 ppm in the water. The source of hydrogen peroxide will typically be present at levels of at least 50 ppm.

By "effective amount" herein is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance cleaning of a soiled surface. Likewise, the term "catalytically effective amount" refers to an amount which is sufficient under whatever comparative test conditions are employed, to enhance cleaning of a soiled surface.

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

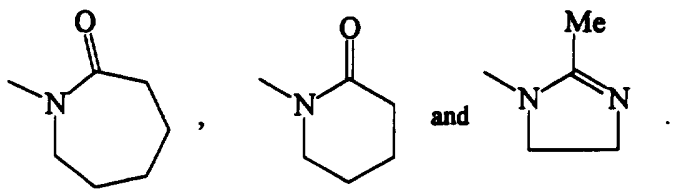
## DETAILED DESCRIPTION OF THE INVENTION

The present invention includes bleach additives and bleaching compositions comprising particularly selected bleach activators collectively referred to as "performance-enhanced bleach activators". The present invention further includes novel bleach activator compounds which are a preferred sub-group of these activators. The bleaching compositions herein, in general, comprise a source of bleach, typically a source of hydrogen peroxide, in addition to the activator component. The bleach additive compositions, however, may or may not have a hydrogen peroxide source built into the formulation. Whereas additive compositions are generally used in conjunction with conventional bleach-containing detergents, especially those formulated with sodium perborate or percarbonate, bleaching compositions according to the invention are typically used as "stand-alone" formulations delivering a full range of cleaning and bleaching effects.

As noted, preferred performance-enhanced bleach activators herein comprise one or more RC(O)- and -L moieties. In general, more than one of each of these can be present. Preferably, one of each is present, and they are covalently connected.

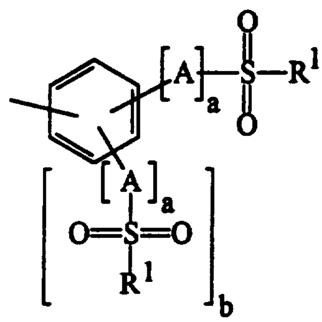
Moieties RC(O) - In preferred bleach activators useful herein, R is nonlimitingly illustrated by electronegatively substituted phenyl selected from the group consisting of p-chlorophenyl, m-chlorophenyl, p-nitrophenyl, 3,5-dichlorophenyl, and 3,5-dinitrophenyl, and mixtures thereof. In yet other preferred embodiments, R is selected from alkylsulfonylphenyl, arylalkylsulfonylphenyl, alkylsulfonyl naphthyl, arylalkylsulfonyl-naphthyl, and mixtures thereof. Note that when naphthyl is selected, unsubstituted 1-naphthyl or substituted 1- or 2-naphthyl is preferred. Other examples of preferred bleach activators include those wherein R is a substituted or unsubstituted furan, and wherein R is substantially free from chloro- or nitro- substituents.

Leaving Groups - The L moieties in the performance-enhanced bleach activators useful in this invention are preferably selected from the group consisting of unsubstituted lactams, substituted lactams, substituted or unsubstituted 2-alkyl 4,5-dihydroimidazoles, and mixtures thereof. Particularly preferred examples of L are those selected from the group consisting of:



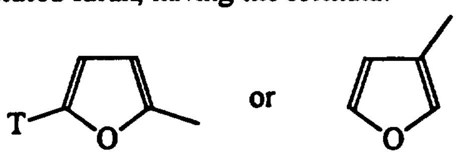
Novel Performance-Enhanced Bleach Activator Compounds - In preferred novel bleach activator compounds of this invention, L is as indicated supra and R is selected from the group consisting of:

(I):



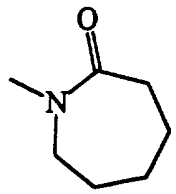
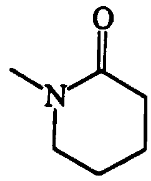
wherein a is independently 0 or 1, b is 0 or 1, A is selected from O and $NR^2$ wherein $R^2$ is H or methyl; when a is 0 or when a is 1 and A is O, $R^1$ is selected from alkyl, arylalkyl, alkoxy, aryloxy, alkylamino, and arylamino; when a is 1 and A is other than O, $R^1$ is selected from alkyl and arylalkyl; and

(II) furan or substituted furan, having the formula:

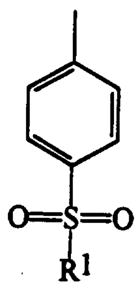
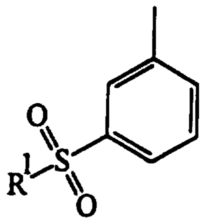
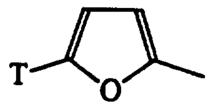
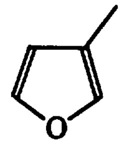


wherein T is selected from the group consisting of H, $NO_2$, Br, alkyl, and arylalkyl.

In a highly preferred embodiment of the performance boosting bleach activator, L is preferably selected from the group consisting of:

 or  ;

and R is selected from the group consisting of:

 ,  ,  or 

wherein R1 is selected from alkyl, arylalkyl, alkoxy, aryloxy, alkylamino, and arylamino; and T is selected from the group consisting of H, Br, and $NO_2$. Compositions comprising these novel compounds are also included in the scope of this invention.

<u>$pK_a$, Rate and Perhydrolysis Criticalities</u> - In accordance with the present invention, there are provided bleaching compositions wherein the bleach activators are required to respect criticalities of $pK_a$ and criticalities relating to rates of perhydrolysis, hydrolysis and diacylperoxide formation. Furthermore, perhydrolysis effciency is important in selecting the bleach activator. All of these criticalities will be better understood and appreciated in light of the following disclosure.

<u>$pK_a$ Value</u> - The acids in which organic chemists have traditionally been interested span a range, from the weakest acids to the strongest, of about 60 pK units. Because no single solvent is suitable over such a wide range, establishment of comprehensive scales of acidity necessitates the use of several different solvents. Ideally, one might hope to construct a universal acidity scale by relating results obtained in different solvent systems to each other. Primarily because solute–solvent interactions affect acid–base equilibria diffently in different solvents, it has not proven possible to establish such a scale.

Water is taken as the standard solvent for establishing an acidity scale. It is convenient, has a high dielectric constant, and is effective at solvating ions.

Equilibrium acidities of a host of compounds (e.g., carboxylic acids and phenols) have been determined in water. Compilations of pK data may be found in Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965 and Supplement, 1973; Serjeant, E. P.; Dempsey, B. "Ionisation Constants of Organic Acids in Aqueous Solution"; 2nd ed., Pergammon Press: Oxford, 1979. Experimental methods for determining $pK_a$ values are described in the original papers. The $pK_a$ values that fall between 2 and 10 can be used with a great deal of confidence; however, the further removed values are from this range, the greater the degree of skepticism with which they must be viewed.

For acids too strong to be investigated in water solution, more acidic media such as acetic acid or mixtures of water with perchloric or sulfuric acid are commonly employed; for acids too weak to be examined in water, solvents such as liquid ammonia, cyclohexylamine and dimethylsulfoxide have been used. The Hammett $H_0$ acidity function has allowed the aqueous acidity scale, which has a practical $pK_a$ range of about 0–12, to be extended into the region of negative $pK_a$ values by about the same range. The use of $H_-$ acidity functions that employ strong bases and cosolvents has similarly extended the range upward by about 12 $pK_a$ units.

The present invention involves the use of leaving groups the conjugate acids of which are considered to be weak; they possess aqueous $pK_a$ values greater than about 13. To establish only that a given compound has an aqueous $pK_a$ above about 13 is straightforward. As noted above, values much above this are difficult to measure with confidence without resorting to the use of an acidity function. The measurement of the acidity of weak acids using the $H_-$ method, which has the advantage of an aqueous standard state, is suitable for determining if the conjugate acid, HL, of leaving group, L, has an aqueous pKa of greater than about 13 to less than about 17. Hovever, it is restricted in that (1) it requires extrapolation across varying solvent media and (2) errors made in determining indicator $pK_a$ values are cumulative. For these and other reasons, Bordwell and co-workers have developed a scale of acidity in dimethylsulfoxide (DMSO). This solvent has the advantage of a relatively high dielectric constant ($\varepsilon = 47$); ions are therefore dissociated so that problems of differential ion pairing are reduced. Although the results are referred to a standard state in DMSO instead of in water, a link with the aqueous $pK_a$ scale has been made. When acidities measured in water or on a water-based scale are compared with those measured in DMSO, acids whose conjugate bases have their charge localized are stronger acids in water; acids whose conjugate bases have their charge delocalized over a large area are usually of comparable strength. Bordwell details his findings in a 1988 article (*Acc. Chem. Res.* 1988, *21*, 456-463). Procedures for measurement of $pK_a$ in DMSO are found in papers referenced therein.

Definitions of $k_H$, $k_P$, and $k_D$ - In the expressions given below, the choice of whether to use the concentration of a nucleophile or of its anion in the rate equation was made as a matter of convenience. One skilled in the art will realize that measurement of solution pH provides a convenient means of directly measuring the concentration of hydroxide ions present. One skilled in the art will further recognize that use of the total concentrations of hydrogen peroxide and peracid provide the most convenient means to determine the rate constants $k_P$ and $k_D$.

The terms, such as RC(O)L, used in the following definitions and in the conditions for the determination of $k_H$, $k_P$ and $k_D$, are illustrative of a general bleach activator structure and are not limiting to any specific bleach activator structure herein.

Definition of $k_H$

$$RC(O)L + HO^- \rightarrow RC(O)O^- + HL$$

The rate of the reaction shown above is given by

$$\text{Rate} = k_H[RC(O)L][HO^-]$$

The rate constant for hydrolysis of bleach activator ($k_H$) is the second order rate constant for the bimolecular reaction between bleach activator and hydroxide anion as determined under the conditions specified below.

Definition of $k_P$

$$RC(O)L + H_2O_2 \rightarrow RC(O)O_2H + HL$$

The rate of the reaction shown above is given by

$$\text{Rate} = k_P[RC(O)L][H_2O_2]_T$$

where $[H_2O_2]_T$ represents the total concentration of hydrogen peroxide and is equal to $[H_2O_2] + [HO_2^-]$.

The rate constant for perhydrolysis of bleach activator ($k_P$) is the second order rate constant for the bimolecular reaction between bleach activator and hydrogen peroxide as determined under the conditions specified below.

Definition of $k_D$

$$RC(O)L + RC(O)O_2H \rightarrow RC(O)O_2C(O)R + HL$$

The rate of the reaction shown above is given by

$$Rate = k_{D'}[RC(O)L][RC(O)O_2H]_T$$

where $[RC(O)O_2H]_T$ represents the total concentration of peracid and is equal to $[RC(O)O_2H] + [RC(O)O_2^-]$.

The rate constant for the formation of a diacylperoxide from the bleach activator ($k_D$), the second order rate constant for the bimolecular reaction between bleach activator and peracid anion, is calculated from the above defined $k_{D'}$. The value for $k_{D'}$ is determined under the conditions specified below.

Conditions for the Determination of Rate Constants

Hydrolysis - A set of experiments is completed to measure the rate of hydrolysis of a bleach activator RC(O)L in aqueous solution at total ionic strength of 1M as adjusted by addition of NaCl. The temperature is maintained at 35.0 ± 0.1 °C and the solution is buffered with $NaHCO_3 + Na_2CO_3$. A solution of the activator ([RC(O)L] = 0.5 mM) is reacted with varying concentrations of NaOH under stopped-flow conditions and the rate of reaction is monitored optically. Reactions are run under pseudo first-order conditions to determine the bimolecular rate constant for hydrolysis of bleach activator ($k_H$). Each kinetic run is repeated at least five times with about eight different concentrations of hydroxide anions. All kinetic traces give satisfactory fits to a first-order kinetic rate law and a plot of the observed first-order rate constant versus concentration of hydroxide anion is linear over the region investigated. The slope of this line is the derived second order rate constant $k_H$.

Perhydrolysis - A set of experiments is completed to measure the rate of perhydrolysis of a bleach activator RC(O)L in aqueous solution at pH = 10.0 with constant ionic strength of 1M as adjusted by addition of NaCl. The temperature is maintained at 35.0 ± 0.1 °C and the solution is buffered with $NaHCO_3 + Na_2CO_3$. A solution of the activator ([RC(O)L] = 0.5 mM) is reacted with varying concentrations of sodium perborate under stopped-flow conditions and the rate of reaction is monitored optically. Reactions are run under pseudo first-order conditions in order to determine the bimolecular rate constant for perhydrolysis of bleach activator (kp). Each kinetic run is repeated at least five times with about eight different concentrations of sodium perborate. All kinetic traces give satisfactory fits to a first-order kinetic rate law and a plot of the observed first-order rate constant versus total concentration of hydrogen peroxide is linear over the region investigated. The slope of this line is the derived second order rate constant kp. One skilled in the art recognizes that this rate constant is distinct from, but related to, the second order rate constant for the reaction of a bleach activator with the anion of hydrogen peroxide ($k_{nuc}$). The relationship of these rate constants is given by the following equation:

$$k_{nuc} = kp\ \{(K_a + [H^+])/K_a\}$$

where $K_a$ is the acid dissociation constant for hydrogen peroxide.

<u>Formation of diacylperoxide</u> - A set of experiments is completed to measure the rate of formation of a diacylperoxide $RC(O)O_2C(O)R$ from a bleach activator RC(O)L in aqueous solution at pH = 10.0 with constant ionic strength of 1M as adjusted by addition of NaCl. The temperature is maintained at 35.0 ± 0.1 °C and the solution is buffered with $NaHCO_3$ + $Na_2CO_3$. A solution of the activator ([RC(O)L] = 0.5 mM) is reacted with varying concentrations of peracid under stopped-flow conditions and the rate of reaction is monitored optically. Reactions are run under pseudo first-order conditions in order to determine the bimolecular rate constant $k_{D'}$. Each kinetic run is repeated at least five times with about eight different concentrations of peracid anion. All kinetic traces give satisfactory fits to a first-order kinetic rate law and a plot of the observed first-order rate constant versus total concentration of peracid is linear over the region investigated. The slope of this line is the derived second order rate constant $k_{D'}$. The bimolecular rate constant for the formation of a diacylperoxide from peracid anion ($k_D$) is calculated according to

$$k_D = k_{D'}\ \{(K_a + [H^+])/K_a\}$$

where $K_a$ is the acid dissociation constant for the peracid $RC(O)O_2H$. One skilled in the art will realize that the $pK_a$ values for peracids fall into a rather narrow range from about 7 to about 8.5 and that at pH = 10.0, when $K_a \geq$ about $10^{-8}$, $\{(K_a + [H^+])/K_a\} \cong 1$ and $k_D \cong k_{D'}$.

Test for Low pH Perhydrolysis Efficiency - This method is applicable as a test for screening any bleach activators RC(O)L (not intending to be limiting of any specific performance-enhanced bleach activator structure herein) by confirmation of the formation of peracid analyte $RC(O)O_2H$. The minimum standard for low pH perhydrolysis efficiency (LPE) is a coefficient, as defined below, ≥ 0.15 within 10 minutes when tested under the conditions specified below.

Test Protocol - Distilled, deionized water (495 mL; adjusted to pH 7.5 with $NaH_2PO_4$ and $Na_2HPO_4$) is added to a 1000 mL beaker and heated to 40 ± 1 °C. Three hundred seventy-five (375) mg of 30% concentration hydrogen peroxide is added to the beaker and the mixture is stirred for two minutes before a 5 mL solution containing 100 mg of activator (predissolved in 5 mL of an organic solvent (e.g. methanol or dimethylformamide)) is added. The initial data point is taken 1 minute thereafter. A second sample is removed at 10 minutes. Sample aliquots (2 mL) are examined via analytical HPLC for the quantitative determination of peracid $RC(O)O_2H$.

Sample aliquots are individually mixed with 2 mL of a pre-chilled 5 °C solution of acetonitrile/acetic acid (86/14) and placed in temperature controlled 5 ° C autosampler for subsequent injection onto the HPLC column.

High performance liquid chromatography of the authentic peracid under a given set of conditions establishes the characteristic retention time ($t_R$) for the analyte. Conditions for the chromatography will vary depending on the peracid of interest and should be chosen so as to allow baseline separation of the peracid from other analytes. A standard calibration curve (peak area vs. concentration) is constructed using the peracid of interest. The analyte peak area of the 10 minute sample from the above described test is thereby converted to ppm peracid generated for determination of the quantity LPE. A bleach activator is considered acceptable when a value of the low pH perhydrolysis efficiency coefficient, LPE = [(ppm of peracid generated)/(theoretical ppm peracid)] ≥ 0.15 is achieved within ten minutes under the specified test conditions.

To note, by comparison with 4,5-saturated cyclic amidine embodiments of the instant bleach activators, known closely related chemical compounds wherein the 4,5 position is unsaturated have surprisingly greater rates of hydrolysis. Specifically, acetyl imidazole has $k_H$ greater than 10.0 $M^{-1}$ $s^{-1}$; accordingly this invention does not encompass imidazole as a leaving group.

Bleaching Compositions - Effective bleach-additives herein may comprise the bleach activators of this invention without a hydrogen peroxide source, but pereferably include detergent surfactants and one or more members selected from the group consisting of low-foaming automatic dishwashing surfactants, ethoxylated nonionic surfactants, bleach stable thickeners, transition-metal chelants, builders, flourescent whitening agents (also known as brighteners), and buffering agents. However, for bleaching compositions, the bleach activators herein are not preferably employed alone but in combination with a source of hydrogen peroxide, as disclosed hereinafter. Levels of the bleach activators herein may vary widely, e.g., from about 0.1% to about 90%, by weight, of composition, although lower levels, e.g., from about 0.1% to about 30% are more typically used.

Source of hydrogen peroxide - A source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen peroxide. Levels may vary widely and are typically from about 0.5% to about 70%, more typically from about 0.5% to about 25%, by weight of the bleaching compositions herein.

The source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Fully-formulated laundry and automatic dishwashing compositions typically will also comprise other adjunct ingredients to improve or modify performance.

Typical, non-limiting examples of such ingredients are disclosed hereinafter for the convenience of the formulator.

Adjunct Ingredients

Bleach catalysts - If desired, the bleaches can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}\text{-}Mn^{IV}_4\text{-}(u\text{-}O)_1(u\text{-}OAc)_2\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclo-nonane})_2\text{-}(ClO_4)_3$, $Mn^{IV}\text{-}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclo-nonane})\text{-}(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Said manganese can be precomplexed with ethylenediaminedisuccinate or separately added, for example as a sulfate salt, with ethylenediaminedisuccinate. (See U.S. Application Ser. No. 08/210,186, filed March 17, 1994.) Other preferred transition metals in said transition-metal-containing bleach catalysts include iron or copper.

Remarkably, preferred embodiments of the present invention in which the wash pH is in the range from about 6.5 to about 9.5 and there is present one of the above-indicated selected performance-enhanced bleach activators in combination with one of the above-indicated bleach catalysts, secure a particularly superior bleaching effect as compared with otherwise identical compositions in which conventional bleach activators such as TAED (see hereinbelow) are used in place of the performance-enhanced bleach activator.

As a practical matter, and not by way of limitation, the bleaching compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 50 ppm, of the catalyst species in the laundry liquor.

Conventional Bleach Activators - "Conventional bleach activators" herein are any bleach activators which do not respect the above-identified provisions given in connection with the performance-boosting bleach activators. Numerous conventional bleach activators are known and are optionally included in the instant bleaching compositions. Various nonlimiting examples of such activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylenediamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical conventional bleach activators. Known amido-derived bleach activators are those of the formulae: $R^1N(R^5)C(O)R^2C(O)L$ or $R^1C(O)N(R^5)R^2C(O)L$ wherein $R^1$ is an alkyl group containing from about 6 to about 12 carbon atoms, $R^2$ is an alkylene containing from 1 to about 6 carbon atoms, $R^5$ is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. Further illustration of optional, conventional bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551. Another class of conventional bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990. Still another class of conventional bleach activators includes those acyl lactam activators which do not provide the benefits and criticalities described herein. Examples of optional lactam activators include octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof.

Bleaching agents other than hydrogen peroxide sources are also known in the art and can be utilized herein as adjunct ingredients. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonated zinc phthalocyanine.

Organic Peroxides, especially Diacyl Peroxides - are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. Suitable organic peroxides, especially diacyl peroxides, are further illustrated in "Initiators for Polymer Production", Akzo Chemicals Inc., Product Catalog, Bulletin No. 88-57, incorporated by reference. Preferred diacyl peroxides herein whether in pure or formulated form for granule, powder or tablet forms of the bleaching compositions constitute solids at 25°C , e.g., CADET® BPO 78 powder form of dibenzoyl peroxide, from Akzo. Highly preferred organic peroxides, particularly the diacyl peroxides, for such bleaching compositions have melting points above 40°C, preferably above 50°C. Additionally, preferred are the organic peroxides with SADT's (as defined in the foregoing Akzo publication) of 35°C or higher, more preferably 70°C or higher. Nonlimiting examples of diacyl peroxides useful herein include dibenzoyl peroxide, lauroyl peroxide, and dicumyl peroxide. Dibenzoyl peroxide is preferred. In some instances, diacyl peroxides are available in the trade which contain oily substances such as dioctyl phthalate. In general, particularly for automatic dishwashing applications, it is preferred to use diacyl peroxides which are substantially free from oily phthalates since these can form smears on dishes and glassware.

Quaternary Substituted Bleach Activators - The present compositions can optionally further comprise conventional, known quaternary substituted bleach activators (QSBA). QSBA's are further illustrated in U.S. 4,539,130, Sept. 3, 1985 and U.S. Pat. No. 4,283,301. British Pat. 1,382,594, published Feb. 5, 1975, discloses a class of QSBA's optionally suitable for use herein. U.S. 4,818,426 issued Apr. 4., 1989 discloses another class of QSBA's. Also see U.S. 5,093,022 issued March 3, 1992 and U.S. 4,904,406, issued Feb. 27, 1990. Additionally, QSBA's are described in EP 552,812 A1 published July 28, 1993, and in EP 540,090 A2, published May 5, 1993.

Detersive Surfactants --Surfactants are useful herein for their usual cleaning power and may be included in preferred embodiments of the instant compositions at the usual detergent-useful levels. Such combinations are better than the surfactant-free counterparts in terms of overall cleaning and bleaching performance and are possibly synergistic.

Nonlimiting examples of surfactants useful herein include the conventional $C_{11}$-$C_{18}$ alkylbenzene sulfonates ("LAS") and primary, branched-chain and random $C_{10}$-$C_{20}$ alkyl sulfates ("AS"), the $C_{10}$-$C_{18}$ secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)CH_3$ and $CH_3(CH_2)_y(CHOSO_3^-M^+)$ $CH_2CH_3$ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the $C_{10}$-$C_{18}$ alkyl alkoxy sulfates ("$AE_xS$"; especially EO 1-7 ethoxy sulfates), $C_{10}$-$C_{18}$ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the $C_{10}$-$C_{18}$ glycerol ethers, the $C_{10}$-$C_{18}$ alkyl polyglycosides and their corresponding sulfated polyglycosides, and $C_{12}$-$C_{18}$ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the $C_{12}$-$C_{18}$ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and $C_6$-$C_{12}$ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxylate/propoxylates), $C_{12}$-$C_{18}$ betaines and sulfobetaines ("sultaines"), $C_{10}$-$C_{18}$ amine oxides, and the like, can also be included in the overall compositions. The $C_{10}$-$C_{18}$ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the $C_{12}$-$C_{18}$ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as $C_{10}$-$C_{18}$ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl $C_{12}$-$C_{18}$ glucamides can be used for low sudsing. $C_{10}$-$C_{20}$ conventional soaps may also be used. If high sudsing is desired, the branched-chain $C_{10}$-$C_{16}$ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Automatic dishwashing compositions typically employ low sudsing surfactants, such as the mixed ethyleneoxy/propyleneoxy nonionics. Other conventional useful surfactants are listed in standard texts.

<u>Builders</u> - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in automatic dishwashing and fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. High performance compositions typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not excluded.

Inorganic or P-containing 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 meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders. See U.S. Pat. 4,605,509 for examples of preferred aluminosilicates.

Examples of silicate builders are the alkali metal silicates, particularly those having a $SiO_2$:$Na_2O$ 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. NaSKS-6® is a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 is the $\delta$-$Na_2SiO_5$ morphology form of layered silicate and can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1} \cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the $\alpha$-, $\beta$- and $\gamma$- forms. Other silicates may also be useful, such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Silicates useful in automatic dishwashing (ADD) applications include granular hydrous 2-ratio silicates such as BRITESIL® H20 from PQ Corp., and the commonly sourced BRITESIL® H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

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. Various grades and types of sodium carbonate and sodium sesquicarbonate may be used, certain of which are particularly useful as carriers for other ingredients, especially detersive surfactants.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula: $[M_z(zAlO_2)_y] \cdot xH_2O$ 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. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$ wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. As with other builders such as carbonates, it may be desirable to use zeolites in any physical or morphological form adapted to promote surfactant carrier function, and appropriate particle sizes may be freely selected by the formulator.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt or "overbased". When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the 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 detergency 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 ethylenediaminetetraacetic 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 polycarboxylate builders of particular importance for heavy duty laundry detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

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. Useful succinic acid builders include the $C_5$-$C_{20}$ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also U.S. Patent 3,723,322.

Fatty acids, e.g., $C_{12}$-$C_{18}$ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

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.

Chelating Agents - The compositions herein may also optionally contain one or more iron and/or manganese chelating agents, such as diethylenetriaminepenta acetic acid (DTPA). More generally, chelating agents suitable for use herein can be selected from the group consisting of aminocarboxylates, aminophosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates; other benefits include inorganic film or scale prevention. Other suitable chelating agents for use herein are the commercial DEQUEST® series, and chelants from Monsanto, DuPont, and Nalco, Inc.

Aminocarboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates). Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A highly preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially (but not limited to) the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The trisodium salt is preferred though other forms, such as magnesium salts, may also be useful.

If utilized, especially in ADD compositions, these chelating agents or transition-metal-selective sequestrants will preferably comprise from about 0.001% to about 10%, more preferably from about 0.05% to about 1% by weight of the bleaching compositions herein.

Enzymes - Enzymes can be included in the formulations herein for a wide variety of fabric laundering or other cleaning purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. 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, etc.. 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 about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S as 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).

An especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76 in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +107 and +123 in *Bacillus amyloliquefaciens* subtilisin as described in the patent applications of A. Baeck, C.K. Ghosh, P.P. Greycar, R.R. Bott and L.J. Wilson, entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/136,797 (P&G Case 5040), and "Bleaching Compositions Comprising Protease Enzymes" having U.S. Serial No. 08/136,626.

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.

Cellulases usable in the present invention include both bacterial or fungal cellulases. 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. CAREZYME® (Novo) is especially useful.

Suitable lipase enzymes for detergent use 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 LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes can be 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 compositions are 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. 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 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No.

86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Other Ingredients - Usual detersive ingredients can include one or more other detersive 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 detersive 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 other active ingredients such as dispersant polymers from BASF Corp. or Rohm & Haas; color speckles, anti-tarnish and/or anti-corrosion agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, anti-oxidants, enzyme stabilizing agents, perfumes, solubilizing agents, clay soil remolval/anti-redeposition agents, carriers, processing aids, pigments, solvents for liquid formulations, fabric softeners, static control agents, solid fillers for bar compositions, etc. Dye transfer inhibiting agents, including polyamine N-oxides such as polyvinylpyridine N-oxide can be used. Dye-transfer-inhibiting agents are further illustrated by polyvinylpyrrolidone and copolymers of N-vinyl imidazole and N-vinyl pyrrolidone. If high sudsing is desired, suds boosters such as the $C_{10}$-$C_{16}$ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The $C_{10}$-$C_{14}$ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as $MgCl_2$, $MgSO_4$, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents.

Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-stryl-phenyl)-2H-napthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stil- benes; 4,4'-bis(stryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-stryl-napth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Various detersive ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detersive ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detersive ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detersive function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT® D10, Degussa) is admixed with a proteolytic enzyme solution containing 3%-5% of $C_{13-15}$ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid or gel compositions can contain some water and other fluids as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Certain bleaching compositions herein among the generally encompassed liquid (easily flowable or gel forms) and solid (powder, granule or tablet) forms, especially bleach additive compositions and hard surface cleaning compositions, may preferably be formulated such that the pH is acidic during storage and alkaline during use in aqueous cleaning operations, i.e., the wash water will have a pH in the range from about 7 to about 11.5. Laundry and automatic dishwashing products are typically at pH 7-12, preferably 9 to 11.5. Automatic dishwashing compositions, other than rinse aids which may be acidic, will typically have an aqueous solution pH greater than 7. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art. The compositions are useful from about 5°C to the boil for a variety of cleaning and bleaching operations.

Bleaching compositions in granular form typically limit water content, for example to less than about 7% free water, for best storage stability.

Storage stability of bleach compositions can be further enhanced by limiting the content in the compositions of adventitious redox-active substances such as rust and other traces of transition metals in undesirable form. Certain bleaching compositions may moreover be limited in their total halide ion content, or may have any particular halide, e.g., bromide, substantially absent. Bleach stabilizers such as stannates can be added for improved stability and liquid formulations may be substantially nonaqueous if desired.

The following examples illustrate the bleach activators of the invention, intermediates for making same and bleaching compositions which can be prepared using the bleach activators, but are not intended to be limiting thereof. All materials in Examples I-XXX satisfy the functional limitations herein.

## EXAMPLE I

N-[(4-methylsulfonyl)benzoyl] caprolactam:

All glassware is dried thoroughly, and the reaction kept under an inert atmosphere (argon) at all times.

With stirring, 5.0 g (25.0 mmol) of (4-methylsulfonyl)benzoic acid (Aldrich) and 5.5 mL (75.0 mmol) of thionyl chloride (Aldrich, d=1.631 g/mol) are added to 100 mL tetrahydrofuran (THF - Aldrich, HPLC grade) in a 3-neck round bottom flask equipped with a reflux condenser, addition funnel, and magnetic stirrer. The resulting reaction mixture is heated to reflux and stirred for 16 h. After cooling to room temperature, the solvent and excess thionyl chloride are removed by evaporation under reduced pressure. Recrystallization of the solid residue from toluene followed by drying under vacuum yields (4-methylsulfonyl)benzoyl chloride as a white, crystalline solid.

In a subsequent reaction, 2.33 g (20.6 mmol) of caprolactam (Aldrich) and 2.30 g (22.7 mmol) of triethylamine (Aldrich, d=0.726 g/mol) are added to 50 mL THF (Aldrich, HPLC grade) in a 3-neck round bottom flask equipped with a reflux condenser, addition funnel, and magnetic stirrer. Addition of a solution of 4.50 g (20.6 mmol) of the (4-methylsulfonyl)-benzoyl chloride in 50 mL THF proceeds dropwise over a period of 30 min, and the resulting reaction mixture is heated to reflux and stirred for 16 h. Upon cooling to room temperature, the THF is removed by evaporation under reduced pressure. The solid residue is redissolved in chloroform, and extracted several times with D.I. water. The organic layer is dried over $Na_2SO_4$, filtered, concentrated by removal of solvent, and poured into hexane to precipitate the product. The precipitate is collected by suction filtration, rinsed with hexane, and dried under vacuum to yield N-[(4-methylsulfonyl)benzoyl] caprolactam as a white, crystalline solid.

## EXAMPLE II

N-[(4-methylsulfonyl)benzoyl]valerolactam:

Synthesized as for N-[(4-methylsulfonyl)benzoyl]caprolactam (Example I) using valerolactam (Aldrich) in place of caprolactam.

## EXAMPLE III

N-[(4-ethylsulfonyl)benzoyl]caprolactam:

The synthesis of N-[(4-ethylsulfonyl)benzoyl]caprolactam proceeds as for N-[(4-methylsulfonyl)benzoyl]caprolactam (Example I) using (4-ethylsulfonyl)benzoic acid in place of (4-methylsulfonyl)benzoic acid.

The (4-ethylsulfonyl)benzoic acid can be synthesized from 2-chloropropionic acid and 4-(chlorosulfonyl)benzoic acid according to the procedure of Brown, R. W. *J. Org. Chem.* **1991**, *56*, 4974-4976.

EXAMPLE IV

N-[(4-ethylsulfonyl)benzoyl]valerolactam:

Synthesized as for N-[(4-ethylsulfonyl)benzoyl]caprolactam (Example III) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE V

N-[(4-pentylsulfonyl)benzoyl]caprolactam:

Synthesized as for N-[(4-ethylsulfonyl)benzoyl]caprolactam (Example III) using 2-bromohexanoic acid (Aldrich) in place of 2-chloropropionic acid.

EXAMPLE VI

N-[(4-pentylsulfonyl)benzoyl]valerolactam:

Synthesized as for N-[(4-pentylsulfonyl)benzoyl]caprolactam (Example V) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE VII

N-[(4-heptysulfonyl)benzoyl]caprolactam:

Synthesized as for N-[(4-ethylsulfonyl)benzoyl]caprolactam (Example III) using 2-bromooctanoic acid (Aldrich) in place of 2-chloropropionic acid.

EXAMPLE VIII

N-[(4-heptylsulfonyl)benzoyl]valerolactam:

Synthesized as for N-[(4-heptylsulfonyl)benzoyl]caprolactam (Example VII) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE IX

N-(2-furoyl)valerolactam:

All glassware is dried thoroughly, and the reaction is kept under an inert atmosphere (argon) at all times. With stirring, 20.0 g (0.18 mol) of 2-furoic acid (Aldrich) and 40.0 mL (0.53 mol) of thionyl chloride (Aldrich, d=1.631 g/mol) are added to 300 mL THF (Aldrich, HPLC grade) in a single-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The resulting reaction mixture is heated to reflux and stirred for 16 h. After cooling to room temperature, the solvent and excess thionyl chloride are removed by evaporation under reduced pressure to yield 2-furoyl chloride.

In a subsequent reaction, 9.2 g (92 mmol) of valerolactam (Aldrich) and 14.1 mL (101 mmol) of triethylamine (Aldrich, d=0.726 g/mol) are added to 150 mL THF (Aldrich, HPLC grade) in a 3-neck round bottom flask equipped with a reflux condenser, addition funnel, and magnetic stirrer. Addition of a solution of 12.0 g (92 mmol) of the 2-furoyl chloride in 150 mL THF proceeds dropwise over a period of 30 min, and the resulting reaction mixture is heated to reflux and stirred for 16 h. Upon cooling to room temperature, the THF is removed by evaporation under reduced pressure. The solid residue is redissolved in methylene chloride, and extracted several times with 5% aqueous hydrochloric and then deionized water. The organic layer is dried over $Na_2SO_4$, filtered, concentrated by removal of solvent, and poured into hexane to precipitate the product. The precipitate is collected by suction filtration, rinsed with hexane, and dried under vacuum to yield N-(2-furoyl)valerolactam as a white, crystalline solid.

EXAMPLE X

N-(2-furoyl)caprolactam:

Synthesized as for N-(2-furoyl)valerolactam (Example IX) using caprolactam (Aldrich) in place of valerolactam.

EXAMPLE XI

N-(3-furoyl)caprolactam:

Synthesized as for N-(2-furoyl)caprolactam (Example X) using 3-furoic acid in place of 2-furoic acid.

EXAMPLE XII

N-(3-furoyl)valerolactam:

Synthesized as for N-(3-furoyl)caprolactam (Example XI) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XIII

N-(5-nitro-2-furoyl)caprolactam:

Synthesized as for N-(2-furoyl)caprolactam (Example XI) using 5-nitro-2-furoic acid in place of 2-furoic acid.

EXAMPLE XIV

N-(5-nitro-2-furoyl)valerolactam:

Synthesized as for N-(5-nitro-2-furoyl)caprolactam (Example XIII) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XV

N-(5-bromo-2-furoyl)caprolactam:

Synthesized as for N-(2-furoyl)caprolactam (Example X) using 5-bromo-2-furoic acid in place of 2-furoic acid.

EXAMPLE XVI

N-(5-bromo-2-furoyl)valerolactam:

Synthesized as for N-(5-bromo-2-furoyl)caprolactam (Example XV) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XVII

N-(1-naphthoyl)caprolactam:

Synthesized as for N-(2-furoyl)caprolactam (Example X) using 1-naphthoic acid in place of 2-furoic acid.

EXAMPLE XVIII

N-(1-naphthoyl)valerolactam:

Synthesized as for N-(1-naphthoyl)caprolactam (Example XVII) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XIX

N-(3,5-dinitrobenzoyl)caprolactam:

All glassware is dried thoroughly, and the reaction is kept under an inert atmosphere (argon) at all times. With stirring, 2.33 g (20.6 mmol) of caprolactam (Aldrich) and 2.30 g (22.7 mmol) of triethylamine (Aldrich, d=0.726 g/mol) are added to 100 mL toluene (Aldrich) in a 3-neck round bottom flask equipped with a reflux condenser, addition funnel, and mechanical stirrer, to give a clear, pale yellow solution. Addition of a solution of 4.75 g (20.6 mmol) of 3,5-dinitrobenzoyl chloride (Aldrich) in 100 mL toluene proceeds dropwise over a period of 30 min. The resulting reaction mixture is heated to reflux and stirred for 16 h. Upon cooling to room temperature, the reaction is filtered to remove the triethylamine hydrochloride, and poured into a separatory funnel. After dilution with 300 mL of chloroform, the organic solution is extracted with 5% aq HCl, 5% aq NaOH, and finally D.I. water. The organic layer is dried over $Na_2SO_4$, filtered, and the solvent removed by evaporation under reduced pressure. Recrystallization of the crude product from toluene followed by drying under vacuum yields N-(3,5-dinitrobenzoyl)caprolactam as a light yellow, crystalline solid.

EXAMPLE XX

N-(3,5-dinitrobenzoyl)valerolactam:

Synthesized as for N-(3,5-dinitrobenzoyl)caprolactam (Example XIX) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XXI

N-(3,5-dichlorobenzoyl)caprolactam:

Synthesized as for N-(4-nitrobenzoyl)caprolactam (Example XXIII) using 3,5-dichlorobenzoylchloride (Aldrich) in place of 4-nitrobenzoyl chloride.

EXAMPLE XXII

N-(3,5-dichlorobenzoyl)valerolactam:

Synthesized as for N-(3,5-dichlorobenzoyl)caprolactam (Example XXI) using valerolactam (Aldrich) in place of caprolactam.

Examples XXIII-XXX exemplify methods for synthesizing compounds generically disclosed in prior references.

EXAMPLE XXIII

N-(4-nitrobenzoyl)caprolactam:

All glassware is dried thoroughly, and the reaction is kept under an inert atmosphere (argon) at all times. With stirring, 43.0 g (0.38 mol) of caprolactam (Aldrich) and 58.2 mL (0.42 mol) of triethylamine (Aldrich, d=0.726 g/mol) is added to 150 mL THF (Aldrich, HPLC grade) in a 3-neck round bottom flask equipped with a reflux condenser, addition funnel, and mechanical stirrer, to give a clear, pale yellow solution. Addition of a solution of 70.5 g (0.38 mol) of 4-nitrobenzoyl chloride (Aldrich) in 100 mL THF proceeds dropwise over a period of 1 h. The cloudy, dark yellow reaction mixture is heated to reflux and stirred for 16 h.

Upon cooling to room temperature, the reaction is filtered to remove the triethylamine hydrochloride, and poured into a separatory funnel. After dilution with chloroform, the organic solution is extracted twice 5% aq HCl, twice with 5% aq NaOH, and finally once with neutral D.I. water. The organic layer is dried over $Na_2SO_4$ or $MgSO_4$, filtered, and the solvent removed by evaporation under reduced pressure. Recrystallization of the crude product from toluene followed by drying under vacuum yields N-(4-nitrobenzoyl)caprolactam as a light yellow, crystalline solid.

EXAMPLE XXIV

N-(4-nitrobenzoyl)valerolactam:

Synthesized as for N-(4-nitrobenzoyl)caprolactam (Example XXIII) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XXV

N-(3-nitrobenzoyl)caprolactam:

Synthesized as for N-(4-nitrobenzoyl)caprolactam (Example XXIII) using 3-nitrobenzoyl chloride (Aldrich) in place of 4-nitrobenzoyl chloride.

EXAMPLE XXVI

N-(3-nitrobenzoyl)valerolactam:

Synthesized as for N-(3-nitrobenzoyl)caprolactam (Example XXV) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XXVII

N-(3-chlorobenzoyl)caprolactam:

Synthesized as for N-(4-nitrobenzoyl)caprolactam (Example XXIII) using 3-chlorobenzoyl chloride (Aldrich) in place of 4-nitrobenzoyl chloride.

EXAMPLE XXVIII

N-(3-chlorobenzoyl)valerolactam:

Synthesized as for N-(3-chloroobenzoyl)caprolactam (Example XXVII) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XXIX

N-(4-chlorobenzoyl)caprolactam:

Synthesized as for N-(4-nitrobenzoyl)caprolactam (Example XXIII) using 4-chlorobenzoylchloride (Aldrich) in place of 4-nitrobenzoyl chloride.

EXAMPLE XXX

N-(4-chlorobenzoyl)valerolactam:

Synthesized as for N-(4-chlorobenzoyl)caprolactam (Example XXIX) using valerolactam (Aldrich) in place of caprolactam.

EXAMPLE XXXI

Bleaching compositions having the form of granular laundry detergents are exemplified by the following formulations.

| | A | B | C | D | E |
|---|---|---|---|---|---|
| INGREDIENT | % | % | % | % | % |
| Bleach Activator* | 5 | 5 | 3 | 3 | 8 |
| Sodium Percarbonate | 0 | 0 | 19 | 21 | 0 |

| | | | | | |
|---|---|---|---|---|---|
| Sodium Perborate monohydrate | 21 | 0 | 0 | 0 | 20 |
| Sodium Perborate tetrahydrate | 12 | 21 | 0 | 0 | 0 |
| Tetraacetylethylenediamine | 0 | 0 | 0 | 1 | 0 |
| Nonanoyloxybenzenesulfonate | 0 | 0 | 3 | 0 | 0 |
| Linear alkylbenzenesulfonate | 7 | 11 | 19 | 12 | 8 |
| Alkyl ethoxylate (C45E7) | 4 | 0 | 3 | 4 | 6 |
| Zeolite A | 20 | 20 | 7 | 17 | 21 |
| SKS-6® silicate (Hoechst) | 0 | 0 | 11 | 11 | 0 |
| Trisodium citrate | 5 | 5 | 2 | 3 | 3 |
| Acrylic Acid/Maleic Acid copolymer | 4 | 0 | 4 | 5 | 0 |
| Sodium polyacrylate | 0 | 3 | 0 | 0 | 3 |
| Diethylenetriamine penta(methylene phosphonic acid) | 0.4 | 0 | 0.4 | 0 | 0 |
| DTPA | 0 | 0.4 | 0 | 0 | 0.4 |
| EDDS | 0 | 0 | 0 | 0.3 | 0 |
| Carboxymethylcellulose | 0.3 | 0 | 0 | 0.4 | 0 |
| Protease | 1.4 | 0.3 | 1.5 | 2.4 | 0.3 |
| Lipolase | 0.4 | 0 | 0 | 0.2 | 0 |
| Carezyme | 0.1 | 0 | 0 | 0.2 | 0 |
| Anionic soil release polymer | 0.3 | 0 | 0 | 0.4 | 0.5 |
| Dye transfer inhibiting polymer | 0 | 0 | 0.3 | 0.2 | 0 |
| Carbonate | 16 | 14 | 24 | 6 | 23 |
| Silicate | 3.0 | 0.6 | 12.5 | 0 | 0.6 |
| Sulfate, Water, Perfume, Colorants | to 100 | to 100 | to 100 | to 100 | to 100 |

*Bleach activator according to any of Examples I - XXX

Any of the above compositions is used to launder fabrics under "high soil" conditions. "High soil" conditions are achieved in either of two possible modes. In a first mode, consumer bundles of heavily soiled fabrics can be used, the soil level being sufficiently high that when a portion of the composition is dissolved in the presence of tap-water together with the soiled fabrics in a U.S. domestic washing-machine, the pH of the wash water is in the range from about pH 6.5 to about 9.5, more typically from about 7 to about 9.5. Alternatively, it is convenient for testing purposes when heavily soiled fabrics are unavailable, to use the following procedure:

the pH of the wash bath after dissolution of product and addition of the test fabrics is adjusted using aqueous HCl such that the pH is in the range from about pH 6.5 to about 9.5. The test fabrics are a lightly soiled or clean bundle of consumer fabrics; additional test swatches of fabric comprising bleachable stains are typically added. In general in the present example, the product usage is low, typically about 1000 ppm concentration of product in the wash.

The fabrics are washed at about 40°C with excellent results, particularly with respect to bleaching as compared with otherwise identical compositions in which TAED, NOBS or benzoylcaprolactam are used at equal weight as a replacement for the *-identified bleach activator. In particular, novel performance-enhanced bleach activators such as those of Examples III-XII provide superior results and are highly preferred.

Additional granular laundry detergents having nonionic surfactant systems are exemplified by the following formulations; they are tested as described supra.

| | F | G | H | I |
|---|---|---|---|---|
| INGREDIENT | % | % | % | % |
| Bleach Activator* | 5 | 3 | 6 | 4.5 |
| Sodium Percarbonate | 20 | 21 | 21 | 21 |
| Tetraacetylethylenediamine | 0 | 6 | 0 | 0 |
| Nonanoyloxybenzenesulfonate | 4.5 | 0 | 0 | 4.5 |
| Alkyl ethoxylate (C45E7) | 2 | 5 | 5 | 5 |
| N-cocoyl N-methyl glucamine | 0 | 4 | 5 | 5 |
| Zeolite A | 6 | 5 | 7 | 7 |
| SKS-6® silicate (Hoechst) | 12 | 7 | 10 | 10 |
| Trisodium citrate | 8 | 5 | 3 | 3 |
| Acrylic Acid/Maleic Acid copolymer (partially neutralized) | 7 | 5 | 7 | 8 |
| Diethylenetriamine penta(methylene phosphonic acid) | 0.4 | 0 | 0 | 0 |
| EDDS | 0 | 0.3 | 0.5 | 0.5 |
| Carboxymethylcellulose | 0 | 0.4 | 0 | 0 |
| Protease | 1.1 | 2.4 | 0.3 | 1.1 |

| | | | | |
|---|---|---|---|---|
| Lipolase | 0 | 0.2 | 0 | 0 |
| Carezyme | 0 | 0.2 | 0 | 0 |
| Anionic soil release polymer | 0.5 | 0.4 | 0.5 | 0.5 |
| Dye transfer inhibiting polymer | 0.3 | 0.02 | 0 | 0.3 |
| Carbonate | 21 | 10 | 13 | 14 |
| Sulfate, Water, Perfume, Colorants | to 100 | to 100 | to 100 | to 100 |

*Bleach activator according to any of Examples I to XXX.

## EXAMPLE XXXII

This Example illustrates cleaning compositions having bleach additive form, more particularly, liquid bleach additive compositions in accordance with the invention.

| | A | B | C | D |
|---|---|---|---|---|
| Ingredients | wt % | wt % | wt % | wt % |
| NEODOL 91-10[1] | 6 | 5 | 7 | 4 |
| NEODOL 45-7[1] | 6 | 5 | 5 | 8 |
| NEODOL 23-2[1] | 3 | 5 | 3 | 3 |
| DEQUEST 2060[2] | 0.5 | 0.5 | 1.0 | 1.0 |
| Bleach Activator[3] | 6 | 6 | 4 | 7 |
| Citric Acid | 0.5 | 0.5 | 0.5 | 0.5 |
| NaOH | to pH 4 | to pH 4 | to pH 4 | to pH 4 |
| Hydrogen Peroxide | 7 | 3 | 2 | 7 |
| Water | Balance to 100% | Balance to 100% | Balance to 100% | Balance to 100% |

[1] Alkyl ethoxylate available from The Shell Oil Company.

[2] Commercially available from Monsanto Co.

[3] Bleach Activator according to any of Examples I-XXX.

| | E | F | G |
|---|---|---|---|
| Ingredients | wt % | wt % | wt % |
| Water | to 100% | to 100% | to 100% |
| NEODOL 91-10[1] | 10 | 10 | 10 |
| NEODOL 23-2[1] | 5 | 5 | 5 |

| | | | |
|---|---|---|---|
| DEQUEST 2010[2] | 0.5 | 0.5 | 1.0 |
| Bleach Activator[3] | 4 | 4 | 8 |
| Citric Acid | 0.5 | 0.5 | 0.5 |
| NaOH | to pH 4 | to pH 4 | to pH 4 |
| Hydrogen Peroxide | 7 | 5 | 5 |

[1] Alkyl ethoxylate available from The Shell Oil Company.

[2] Commercially available from Monsanto Co.

[3] Bleach activator according to any of Examples I-XXX.

The compositions are used as bleach boosting additive (to be used in ADDITION to a bleach OR non-bleach detergent such as TIDE®) in a wash test otherwise similar to that used in Example XXXI. The additive is used at 1000 ppm, and the commercial detergent is used at 1000 ppm.

EXAMPLE XXXIII

This Example illustrates cleaning compositions having bleach additive form, more particularly, liquid bleach additive compositions without a hydrogen peroxide source in accordance with the invention.

| | A | B | C | D |
|---|---|---|---|---|
| Ingredients | wt % | wt % | wt % | wt % |
| NEODOL 91-10[1] | 6 | 5 | 7 | 10 |
| NEODOL 45-7[1] | 6 | 5 | 5 | 0 |
| NEODOL 23-2[1] | 3 | 5 | 3 | 5 |
| DEQUEST 2060[2] | 0.5 | 0.5 | 1.0 | 1.0 |
| Bleach Activator[3] | 6 | 6 | 4 | 7 |
| Citric Acid | 0.5 | 0.5 | 0.5 | 0.5 |
| NaOH | to pH 4 | to pH 4 | to pH 4 | to pH 4 |
| Water | Balance to 100% | Balance to 100% | Balance to 100% | Balance to 100% |

[1] Alkyl ethoxylate available from The Shell Oil Company.

[2] Commercially available from Monsanto Co.

[3] Bleach Activator according to any of Examples I-XXX.

The compositions are used as bleach boosting additive (to be used in ADDITION to a bleach detergent such as TIDE® WITH BLEACH) in a wash test otherwise similar to that used in Example XXXI. The additive is used at 1000 ppm, and the commercial detergent is used at 1000 ppm.

EXAMPLE XXXIV

Bleaching compositions having the form of granular laundry detergents are exemplified by the following formulations.

| | A | B | C | D | E |
|---|---|---|---|---|---|
| INGREDIENT | % | % | % | % | % |
| Bleach Activator* | 5 | 5 | 3 | 3 | 8 |
| Sodium Percarbonate | 0 | 5 | 15 | 0 | 0 |
| Sodium Perborate monohydrate | 5 | 0 | 0 | 10 | 20 |
| Brightener 49 | 0.4 | 0.4 | 0 | 0 | 0 |
| NaOH | 2 | 2 | 2 | 0 | 2 |
| Linear alkylbenzenesulfonate, partially neutralized | 9 | 9 | 9 | 9 | 9 |
| Alkyl ethoxylate (C25E9) | 7 | 7 | 5 | 4 | 6 |
| Zeolite A | 32 | 20 | 7 | 17 | 21 |
| Acrylic Acid/Maleic Acid copolymer | 0 | 0 | 4 | 5 | 8 |
| Sodium polyacrylate | 0.6 | 0.6 | 0.6 | 0 | 0 |
| Diethylenetriamine penta(methylene phosphonic acid) | 0.5 | 0 | 0.5 | 0 | 1 |
| EDDS | 0 | 0.5 | 0 | 0.5 | 0 |
| Protease | 1 | 1 | 1.5 | 2.4 | 0.3 |
| Lipolase | 0 | 0 | 0 | 0.2 | 0 |
| Carezyme | 0 | 0 | 0 | 0.2 | 0 |
| Anionic soil release polymer | 0 | 0 | 0.5 | 0.4 | 0.5 |
| Dye transfer inhibiting polymer | 0 | 0 | 0.3 | 0.2 | 0 |
| Soda Ash | 22 | 22 | 22 | 22 | 22 |
| Silicate (2r) | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 |
| Sulfate, Water, Perfume, Colorants | to 100 | to 100 | to 100 | to 100 | to 100 |

*Bleach activator according to any of Examples I - XXX

Any of the above compositions is used to launder fabrics under mildly alkaline conditions (pH 7 - 8). The pH can be adjusted by altering the proportion of acid to Na- salt form of alkylbenzenesulfonate.

Fabrics are washed at about 40°C using a concentration of about 1000 ppm of the composition with excellent results, particularly with respect to bleaching as compared with otherwise identical compositions in which TAED, NOBS or benzoylcaprolactam are used at equal weight as a replacement for the performance-enhanced bleach activator. In particular, novel performance-enhanced bleach activators, such as those of Examples III-XII, provide superior results and are highly preferred.

EXAMPLE XXXV

A cleaning composition designed for use as a granular bleach additive is as follows:

| Ingredient | % (wt.) |
|---|---|
| Bleach Activator* | 7.0 |
| Sodium Perborate (monohydrate) | 20.0 |
| Chelant (DTPA, acid form) | 10.0 |
| Citric Acid (coated) | 20.0 |
| Sodium Sulfate | Balance |

*Bleach Activator according to any of Examples I-XXX.

In an alternate embodiment, the composition is modified by replacing the sodium perborate with sodium percarbonate.

EXAMPLE XXXVI

Cleaning compositions having liquid form especially useful for cleaning bathtubs and shower tiles without being harsh on the hands are as follows:

| Ingredient | % (wt.) | |
|---|---|---|
| | A | B |
| Bleach Activator* | 7.0 | 5.0 |
| Hydrogen Peroxide | 10.0 | 10.0 |
| $C_{12}$AS, acid form, partially neutralized | 5.0 | 5.0 |
| $C_{12-14}AE_3S$, acid form, partially neutralized | 1.5 | 1.5 |
| $C_{12}$ DimethylAmine N-Oxide | 1.0 | 1.0 |
| DEQUEST 2060 | 0.5 | 0.5 |
| Citric acid | 5.5 | 6.0 |
| Abrasive (15-25 micrometer) | 15.0 | 0 |
| HCL | to pH 4 | |
| Filler and water | Balance to 100% | |

*Bleach Activator according to any of Examples I-XXX.

EXAMPLE XXXVII

A granular automatic dishwashing detergent composition comprises the following.

| | A | B | C | D |
|---|---|---|---|---|
| INGREDIENT | wt % | wt % | wt % | wt % |
| Bleach Activator (See Note 1) | 3 | 4.5 | 2.5 | 4.5 |
| Sodium Perborate Monohydrate (See Note 2) | 1.5 | 0 | 1.5 | 0 |
| Sodium Percarbonate (See Note 2) | 0 | 1.2 | 0 | 1.2 |
| Amylase (TERMAMYL® from NOVO ) | 1.5 | 2 | 2 | 2 |
| Dibenzoyl Peroxide | 0 | 0 | 0.8 | 0 |
| Transition Metal Bleach Catalyst (See Note 3) | 0 | 0.1 | 0.1 | 0 |
| Protease (SAVINASE® 12 T, NOVO, 3.6% active protein) | 2.5 | 2.5 | 2.5 | 2.5 |
| Trisodium Citrate Dihydrate (anhydrous basis) | 7 | 15 | 15 | 15 |
| Citric Acid | 14 | 0 | 0 | 0 |
| Sodium Bicarbonate | 15 | 0 | 0 | 0 |
| Sodium Carbonate, anhydrous | 20 | 20 | 20 | 20 |
| BRITESIL H2O®, PQ Corp. (as $SiO_2$) | 7 | 8 | 7 | 5 |
| Diethylenetriaminepenta(methylenephosphonic acid), Na | 0 | 0 | 0 | 0.2 |
| Hydroxyethyldiphosphonate (HEDP), Sodium Salt | 0 | 0.5 | 0 | 0.5 |
| Ethylenediaminedisuccinate, Trisodium Salt | 0.1 | 0.3 | 0 | 0 |
| Dispersant Polymer (Accusol 480N) | 6 | 5 | 8 | 10 |
| Nonionic Surfactant (LF404, BASF) | 2.5 | 1.5 | 1.5 | 1.5 |
| Paraffin (Winog 70®) | 1 | 1 | 1 | 0 |
| Benzotriazole | 0.1 | 0.1 | 0.1 | 0 |
| Sodium Sulfate, water, minors BALANCE TO: | 100% | 100% | 100% | 100% |

Note 1:Bleach Activator according to any of Examples I -XXX.

Note 2: These hydrogen peroxide sources are expressed on a weight % available oxygen basis. To convert to a basis of percentage of the total composition, divide by about 0.15.

Note 3:Transition Metal Bleach Catalyst: MnEDDS according to U.S. Application Ser. No. 08/210,186, filed March 17, 1994.

EXAMPLE XXXVIII

A commercial rinse-aid block sold as "Jet-Dry" is modified as follows: The rinse aid block and about 5% - 20% of a bleach activator according to any of Examples I-XXX are comelted, mixed and resolidified into block form. The resulting cleaning composition is used in an automatic dishwashing appliance with excellent spotting/filming and stain removal results.

EXAMPLE XXXIX

Liquid bleaching compositions for cleaning typical househould surfaces are as follows. The hydrogen peroxide is separated as an aqueous solution from the other components by a suitable means such as a dual chamber container.

| Component | A (wt %) | B (wt %) |
|---|---|---|
| $C_{8-10}E_6$ nonionic surfactant | 20 | 15 |
| $C_{12-13}E_3$ nonionic surfactant | 4 | 4 |
| $C_8$ alkyl sulfate anionic surfactant | 0 | 7 |
| $Na_2CO_3/NaHCO_3$ | 1 | 2 |
| $C_{12-18}$ Fatty Acid | 0.6 | 0.4 |
| Hydrogen peroxide | 7 | 7 |
| Bleach Activator* | 7 | 7 |
| Dequest 2060** | 0.05 | 0.05 |
| $H_2O$ | Balance to 100 | Balance to 100 |

* Bleach Activator according to any of Examples I-XXX.

**Commercially available from Monsanto Co.

EXAMPLE XXXX

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

| Component | Weight % |
|---|---|
| Bleach Activator according to any of Examples I-XXX | 4 |
| Sodium Perborate Tetrahydrate | 12 |
| $C_{12}$ linear alkyl benzene sulfonate | 30 |
| Phosphate (as sodium tripolyphosphate) | 10 |
| Sodium carbonate | 5 |
| Sodium pyrophosphate | 7 |

| | |
|---|---|
| Coconut monoethanolamide | 2 |
| Zeolite A (0.1-10 micron) | 5 |
| Carboxymethylcellulose | 0.2 |
| Polyacrylate (m.w. 1400) | 0.2 |
| Brightener, perfume | 0.2 |
| Protease | 0.3 |
| $CaSO_4$ | 1 |
| $MgSO_4$ | 1 |
| Water | 4 |
| Filler* | Balance to 100% |

*Can be selected from convenient materials such as $CaCO_3$, talc, clay, silicates, and the like. Acidic fillers can be used to reduce pH.

Fabrics are washed with the bar with excellent results.

WHAT IS CLAIMED IS:

1. A cleaning composition comprising an effective amount of one or more performance-enhanced bleach activators having a moiety RC(O)- which produces a peracid RC(O)-OOH on perhydrolysis; wherein R is selected such that the difference in aqueous $pK_a$ between acetic acid and the carboxylic acid analog, RC(O)OH, of said peracid is at least 0.6; said performance-enhanced bleach activator having a low pH perhydrolysis efficiency coefficient of greater than 0.15, preferably greater than 0.3, and a ratio $k_P/k_D \geq 5$, preferably $\geq 50$, wherein $k_P$ is the rate constant for perhydrolysis of the performance-enhanced bleach activator and $k_D$ is the rate constant for the formation of a diacylperoxide from the performance-enhanced bleach activator.

2. A composition according to Claim 1 wherein said performance-enhanced bleach activator is free from any heterocyclic moiety wherein a hydrogen atom is attached to a carbon atom that is *alpha* to both a carbonyl group and a multivalent heteroatom.

3. A composition according to Claim 2 wherein said performance-enhanced bleach activator has the formula RC(O)-L wherein L is a leaving-group comprising at least one tri-coordinate nitrogen atom covalently connecting L to RC(O)-; wherein said performance-enhanced bleach activator is capable of forming a maximum of one mole equivalent of said peracid on perhydrolysis, and wherein said performance-enhanced bleach activator has $k_H \leq 10\ M^{-1}\ s^{-1}$ and a ratio $k_P/k_H \geq 1$, preferably $\geq 2$, wherein $k_H$ is the rate constant for hydrolysis of the performance-enhanced bleach activator and $k_P$ is said rate constant for perhydrolysis.

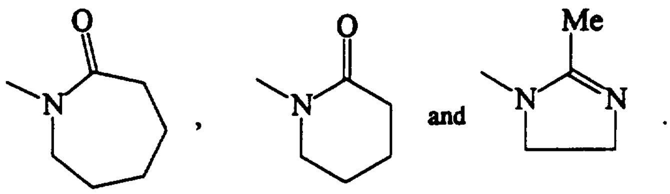
4. A composition according to Claim 3 wherein R is selected such that the difference in aqueous $pK_a$ between said carboxylic acid analog, RC(O)OH, of said peracid and acetic acid is at least 1.2 and L is selected such that its conjugate acid, HL, has an aqueous $pK_a$ in the range from greater than 13 to less than 17.

5. A composition according to Claim 4 further comprising a source of hydrogen peroxide and wherein said composition delivers an aqueous pH in the range from 6.5 to 9.5 and wherein the level of said source of hydrogen peroxide is

sufficient to provide a perhydroxyl ion concentration, as measured at a pH of 7.5, of $10^{-4}$ to $10^{-10}$ molar.

6. A composition according to Claim 5 wherein L is selected from the group consisting of unsubstituted lactams, substituted lactams and substituted or unsubstituted 2-alkyl 4,5-dihydroimidazoles.

7. A composition according to Claim 6 wherein L is selected from the group consisting of:




8. A composition according to Claim 7 wherein R is connected to -C(O)- in said moiety RC(O)- through a carbon atom which forms part of an aromatic ring and wherein R is electronegatively substituted phenyl selected from the group consisting of p-chlorophenyl, m-chlorophenyl, p-nitrophenyl, 3,5-dichlorophenyl, 3,5-dinitrophenyl, alkylsulfonylphenyl, arylalkylsulfonylphenyl, alkylsulfonyl naphthyl and arylalkylsulfonylnaphthyl.

9. A composition according to Claim 8 wherein R is a substituted or unsubstituted furan.

10. A composition according to Claim 8 wherein R is substantially free from chloro- or nitro- substituents.

11. A composition according to Claim 8 wherein L is an unsubstituted caprolactam or valerolactam leaving-group.

12. A composition according to Claim 8 further comprising a member selected from the group consisting of laundry detergent surfactants, low-foaming automatic dishwashing surfactants, bleach-stable thickeners, trnasition-metal chelant, fluorescent whitening agents, and mixtures thereof.

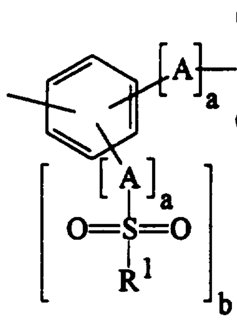
13. A composition according to Claim 12 wherein said laundry detergent surfactants comprises an ethoxylated nonionic surfactant.

14. A composition according to Claim 12 comprising:
from 0.1% to 30% of said performance-enhanced bleach activator;
from 0.1% to 70% of a hydrogen peroxide source; and
from 0.001% to 10% of a transition-metal chelant.

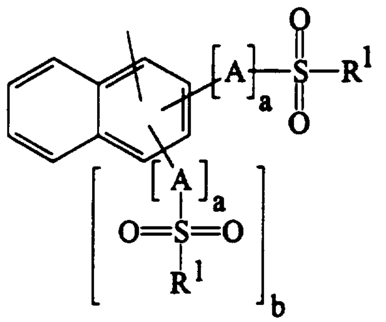
15. A bleach-additive or bleaching composition comprising from 0.1 % to 10% of a performance-enhanced bleach activator selected from the group consisting of: p-nitrobenzoyl caprolactam; p-nitrobenzoylvalerolactam; linear or branched C2-C9 alkylsulfonylbenzoylcaprolactam; linear or branched C2-C9 alkylsulfonylbenzoylvalerolactam; linear or branched C2-C9 alkyloxysulfonylbenzoylcaprolactam; linear or branched C2-C9 alkyloxysulfonyl-benzoylvalerolactam; linear or branched C2-C9 alkyl(amino)sulfonylbenzoylcaprolactam; linear or branched C2-C9 alkyl(amino)sulfonylbenzoylvalerolactam; linear or branched C2-C9 alkylsulfonylnaphthylcaprolactam; linear or branched C2-C9 alkylsulfonylnaphthylvalerolactam; linear or branched C2-C9 alkyloxysulfonylnaphthylcaprolactam; linear or branched C2-C9 alkyloxysulfonylnaphthylvalerolactam; linear or branched C2-C9 alkyl(amino)sulfonylnaphthylcaprolactam; linear or branched C2-C9 alkyl(amino)sulfonylnaphthylvalerolactam; 2-furoylcaprolactam; 2-furoylvalerolactam; 3-furoylcaprolactam; 3-furoylvalerolactam; 5-nitro-2-furoylcaprolactam; 5-nitro-2-furoylvalerolactam; 1-naphthylcaprolactam; 1-naphthylvalerolactam; and mixtures thereof.

16. A composition according to Claim 15 wherein said performance-enhanced bleach activator is selected from the group consisting of:
linear or branched C2-C9 alkylsulfonylbenzoylcaprolactam; linear or branched C2-C9 alkylsulfonylbenzoylvalerolactam; linear or branched C2-C9 alkyloxysulfonylbenzoylcaprolactam; linear or branched C2-C9 alkyloxysulfonylbenzoylvalerolactam; linear or branched C2-C9 alkyl(amino)sul-fonylbenzoylcaprolactam; linear or branched C2-C9 alkyl(amino)sulfonyl-benzoylvalerolactam; 2-furoylcaprolactam; 2-furoylvalerolactam; 3-furoylcaprolactam; 3-furoylvalerolactam; 5-nitro-2-furoyl-caprolactam; 5-nitro-2-furoylvalerolactam; and mixtures thereof.

17. A performance-enhanced bleach activator compound having the formula RC(O)-L: wherein L is selected from the group consisting of lactams and 4,5-dihydroimidazoles and R is selected from the group consisting of substituted phenyl having more than one chloro, bromo or nitro substituent; furan or substituted furan having one or more chloro, bromo, nitro, alkylsulfonyl or arylalkylsulfonyl substituents; 1-naphthyl; substituted 1-naphthyl or substituted 2-naphthyl having one or more chloro, bromo or nitro substituents;



,



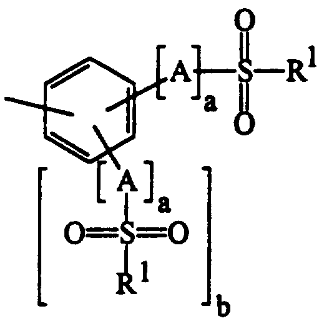
;

and mixtures thereof;

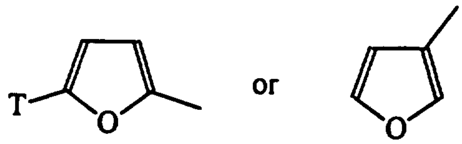
wherein in each structure a is independently 0 or 1, b is 0 or 1, and A is selected from O and $NR^2$ wherein $R^2$ is H or methyl; and wherein when a is 1 and A is O, $R^1$ is selected from alkyl, arylalkyl, alkoxy, aryloxy, alkylamino, and arylamino; when a is 1 and A is other than O, $R^1$ is selected from alkyl and arylalkyl.

18. A compound according to Claim 17 wherein R is selected from the group consisting of:

(I):

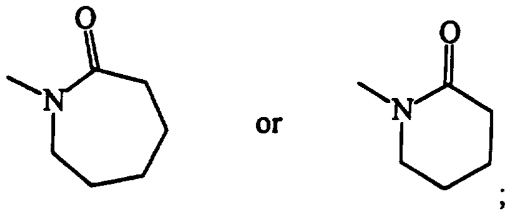



wherein a is independently 0 or 1, b is 0 or 1, A is selected from O and $NR^2$ wherein $R^2$ is H or methyl; when a is 0 or when a is 1 and A is O, $R^1$ is selected from alkyl, arylalkyl, alkoxy, aryloxy, alkylamino, and arylamino; when a is 1 and A is other than O, $R^1$ is selected from alkyl and arylalkyl; and (II) said furan or substituted furan, having the formula:

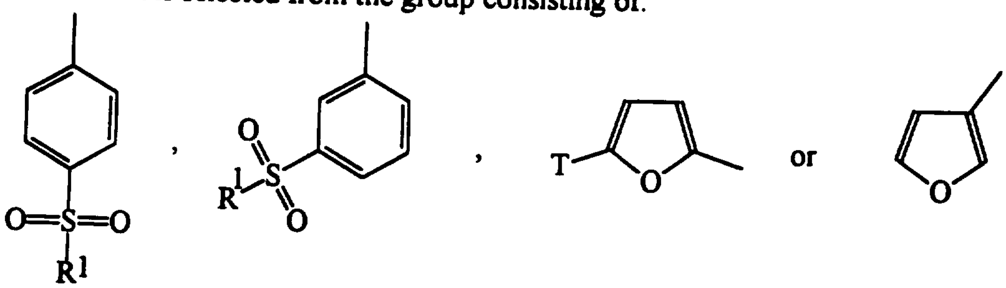


wherein T is selected from the group consisting of H, $NO_2$, Br, alkyl, and arylalkyl.

19. A compound according to Claim 18 wherein L is selected from the group consisting of:



and R is selected from the group consisting of:



wherein $R^1$ is selected from alkyl, arylalkyl, alkoxy, aryloxy, alkylamino, and arylamino; and T is selected from the group consisting of H, Br, and $NO_2$.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/14687

**A. CLASSIFICATION OF SUBJECT MATTER**

C 11 D 3/39

According to International Patent Classification (IPC) or to both national classification and IPC6

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C 11 D

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. |
|---|---|---|
| P,A | WO, A, 94/28 102 (THE PROCTER & GAMBLE) 08 December 1994 (08.12.94), page 5, line 29 - page 8, line 4; examples; claims. -- | 1, 12-19 |
| P,A | WO, A, 94/28 103 (THE PROCTER & GAMBLE) 08 December 1994 (08.12.94), examples; claims. -- | 1, 12-19 |
| P,A | WO, A, 94/28 104 (THE PROCTER & GAMBLE) 08 December 1994 (08.12.94), examples; claims. -- | 1, 12-19 |
| P,A | WO, A, 94/28 105 - (THE PROCTER & GAMBLE) 08 December 1994 (08.12.94), | 1, 12-19 |

[X] 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

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"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

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 21 March 1996 | 19 -04- 1996 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016 | SEIRAFI e.h. |

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| | examples; claims. | |
| P,A | WO, A, 94/28 106 (THE PROCTER & GAMBLE) 08 December 1994 (08.12.94), examples; claims. | 1, 12-19 |
| P,A | WO, A, 95/17 497 (THE PROCTER & GAMBLE) 29 June 1995 (29.06.95), examples; claims. | 1, 12-19 |
| P,A | WO, A, 95/17 498 (THE PROCTER & GAMBLE) 29 June 1995 (29.06.95), the whole document. | 1, 12-19 |
| P,A | WO, A, 95/29 160 (THE PROCTER & GAMBLE) 02 November 1995 (02.11.95), the whole document. | 1, 12-19 |

## ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

## ANNEX

to the International Search Report to the International Patent Application No.

## ANNEXE

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 95/14687 SAE 122947

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

| Im Recherchenbericht angeführtes Patentdokument<br>Patent document cited in search report<br>Document de brevet cité dans le rapport de recherche | Datum der Veröffentlichung<br>Publication date<br>Date de publication | Mitglied(er) der Patentfamilie<br>Patent family member(s)<br>Membre(s) de la famille de brevets | Datum der Veröffentlichung<br>Publication date<br>Date de publication |
|---|---|---|---|
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