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BLEACHING DETERGENT LIQUORS INCORPORATING NON
LINEAR PEROXYCARBOXYLIC ACID PRECURSORS AND
COMPOSITIONS FOR USE THEREIN

Field of the Invention

This invention relates to the field of oxidisable stain removal, especially but not solely to the removal of oxidisable stains from fabrics and is particularly concerned with the removal of these stains using peroxygen bleaches at temperatures $< 60^{\circ}\text{C}$ such as are encountered in domestic washing and laundering operations.

Background to the Invention

The removal of oxidisable stains from either hard surfaces or fabrics by means of peroxygen bleaches at temperatures less than 60°C is a well known technique and customarily involves the use of organic peroxy acids. The most commonly used peroxy acid is peracetic acid, normally generated in situ in the bleaching or laundry liquor by the reaction of alkaline hydrogen peroxide with a peroxy acid

precursor (the so-called bleach activator). However, peroxyacids containing more than 2 carbon atoms in the acyl group have also been disclosed and taught for this purpose and BP 864,798, Canadian Patent No. 635,620, US Patent Nos. 4100095, 4119660, 4126573 and European Published Application No. 0068547 all relate to the formation, stabilisation or use of such materials.

Recently, as described in European Application No. 0068547, it has been found that selection of the chainlength of the aliphatic moiety of the peroxy acid permits the peroxy acid to be concentrated in the area where stain removal is required. Thus for removal of fugitive dyestuffs in bulk solution, a 'hydrophilic' bleach species is satisfactory, whereas for stains on solid surfaces a bleaching species showing more hydrophobic character, and hence a tendency to migrate to the solid-liquid interface, may be more beneficial.

In the commonly assigned US Patent No. 4412934 issued to Stanley Y Chung & Gianfranco L Spadini, on November 1st 1983 entitled "Bleaching Compositions", and Published European Application No. 0098129 entitled "Detergent Additive Product" compositions are disclosed which incorporate a C_8-C_{10} acyloxy compound capable of forming a C_8-C_{10} aliphatic peroxy acid on reaction with alkaline hydrogen peroxide, the C_8-C_{10} acyl group being linear in nature.

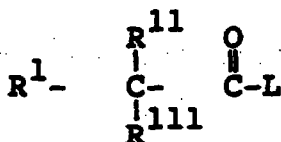
Although compositions prepared in accordance with these last named disclosures provide superior stain removal performance to prior art products employing peracetic acid or its precursors, it has been found that, under certain conditions, odours produced in the wash solution by these products are aesthetically

unattractive.

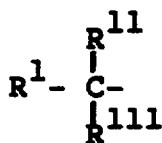
It has now been found that certain branched chain aliphatic peroxy acid precursors, when added to aqueous liquors containing a source of alkaline hydrogen peroxide, provide effective bleaching of oxidisable stains, particularly at temperatures at or below 60°C without generating aesthetically unattractive odours. The precursor compounds can be added to such liquors on their own, or added to water as part of a complete inorganic peroxy bleach-containing detergent composition or as part of a laundry additive product added to an aqueous solution of an inorganic peroxy bleach-containing detergent composition.

Summary of the Invention

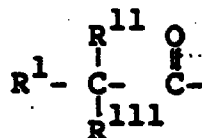
According to one aspect of the invention therefore there is provided an aqueous laundry bleaching liquor having a bland odour comprising a source of alkaline hydrogen peroxide in an amount of from 50 to 350 ppm together with a non-linear substituted or unsubstituted peroxyalkanoic acid precursor in an amount to give from 1 to 50 ppm of the peroxyalkanoic acid upon reaction with said alkaline hydrogen peroxide source, said precursor having the general formula:



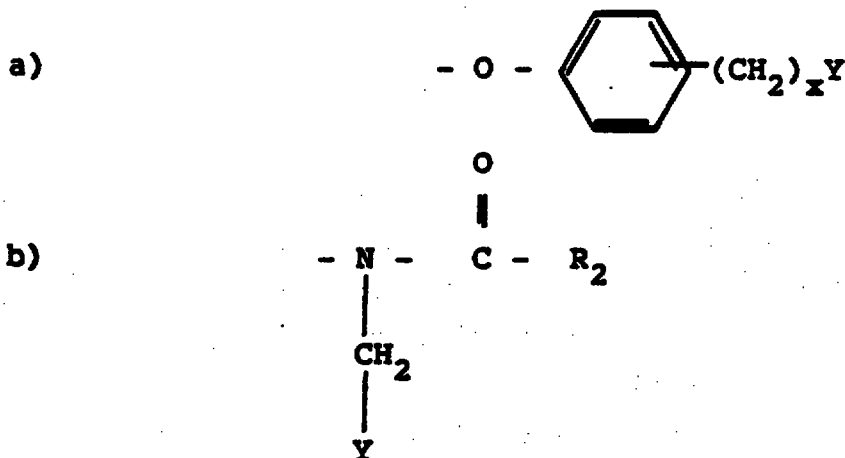
wherein R_1 is a hydrocarbyl moiety which may also incorporate heteroatoms provided that such heteroatoms are pendant therefrom, the group:



being an organic moiety of non-linear structural configuration selected from aliphatic, cycloaliphatic, and aryl aliphatic, at least one of R^{11} and R^{111} being hydrogen, the other of R^{11} and R^{111} being independently selected from hydrogen and C_1 - C_4 alkyl groups, the group:



being the acyl moiety of a non linear substituted or unsubstituted alkanolic acid having a $\log P_{OCT}$ of from 1.9 to 4.1, wherein P_{OCT} is the partition coefficient of the alkanolic acid between n-octanol and water at 21°C, and L is a leaving group selected from:



wherein R_2 is an alkyl group containing from 1 to 4 carbon atoms, x is 0 or an integer from 1 to 4 and Y is selected from:

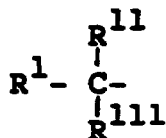
- SO_3M
- OSO_3M
- CO_2M
- $N^+(R_2)_3Q^-$
- $N(R_2)_2 \rightarrow O$

wherein M is H, alkali metal, alkaline earth metal, ammonium or substituted ammonium, and Q is a halide or methosulphate, the conjugate acid of said leaving group L having a pK_a in the range from 6 to 13.

These leaving groups have a pK_a more preferably in the range from 7 to 11, most preferably from 8 to 10.

Preferred leaving groups are those of formula a) above in which x is 0 and Y is selected from $-SO_3M$ and $-CO_2M$ wherein M is alkali metal, preferably sodium.

Preferably the group:



is a C_7-C_9 alkyl group and preferred compounds are alkali metal, ammonium or substituted ammonium 2-ethyl hexanoyl oxybenzene sulphonates and 3,5,5-trimethyl hexanoyl oxybenzene sulphonates, with sodium being the preferred cation.

The present invention embraces the formation of aqueous bleaching liquors by means of the reaction of a source of alkaline hydrogen peroxide with additive products containing precursors of an aliphatic peroxy

acid whose carboxylic acid analogue has a $\log P_{OCT}$ of from 1.9 to 4.1, particularly with the C_6-C_{16} branched alkyl group-containing precursor compounds specifically described herein, or by means of the addition of detergent or bleaching compositions containing such precursor compounds to an aqueous medium. Aqueous bleaching liquors in accordance with the invention develop low intensity or bland odours which are compatible with and/or are capable of being masked by the perfume compositions conventionally used in detergent products. Aqueous bleaching liquors containing the most highly preferred compounds are virtually odourless whereas the analogous linear alkyl chain materials have a pungent odour which is aesthetically undesirable.

According to another aspect of the invention, solid laundry bleaching compositions adapted to form an aqueous laundry bleaching liquor are provided comprising a non linear substituted or unsubstituted peroxyalkanoic acid precursor having a general formula as recited above, together with an alkali metal inorganic peroxyhydrate salt or a hydrogen peroxide clathrate. In a further embodiment, such laundry bleaching compositions are provided comprising the peroxyalkanoic acid precursor, as above defined, in combination with a surfactant which may be anionic, nonionic, cationic or zwitterionic or a mixture thereof and a source of alkaline hydrogen peroxide. In a preferred form of this aspect of the invention, the surfactant is a mixture which is primarily anionic in character with nonionic and, in a highly preferred form, cationic components. Also in a preferred form of the invention, the molar ratio of the hydrogen

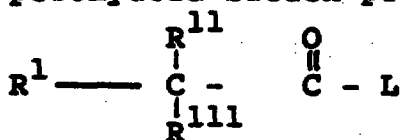
peroxide present to the peroxyalkanoic acid precursor is at least 1.5:1.

In a further aspect of the invention, laundry additive products adapted for addition to an aqueous laundry liquor are provided in which a non linear peroxy alkanoic acid precursor as hereinabove defined, is enclosed in a container such as a bag or pouch of synthetic polymeric film material, which is formed with a water frangible closure to permit release of its contents on immersion in an alkaline aqueous laundry liquor containing a source of hydrogen peroxide. Another form of this aspect of the invention comprises a precursor as defined above in water-releasable combination with a flexible non-particulate substrate in a precursor:substrate weight ratio of 1:10 to 30:1. In both of these additive compositions other detergent components, such as surfactants, builder salts and chelating agents, may be present.

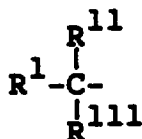
Another aspect of the invention comprises a method of forming an aqueous laundry liquor having a bland odour by the addition of laundry additive compositions as defined above to aqueous solutions containing a source of alkaline hydrogen peroxide.

Detailed Description of the Invention

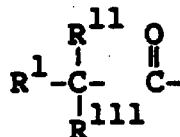
The compounds found to be useful as organic peroxyacid bleach precursors have the formula



wherein the group:



is an organic moiety of non-linear structural configuration, at least one of R^{11} and R^{111} being hydrogen, the other of R^{11} and R^{111} being independently selected from hydrogen and C_1-C_4 alkyl groups, the group:



being the acyl moiety of a carboxylic acid having as $-\log P_{OCT}$ of from 1.9 to 4.1, wherein P_{OCT} is the partition coefficient of the carboxylic acid between n-octanol and water at 21°C; and L is a leaving group, the conjugate acid of which has a pKa in the range from 6 to 13.

R^1 is an organic moiety which may be purely aliphatic in nature with a linear, cycloaliphatic or branched structure or alternatively may be an aryl aliphatic moiety. R^1 may also include heteroatoms such as oxygen, nitrogen and halogen provided these are not in the backbone of the group i.e. they must be pendant from the hydrocarbyl structure. Groups subject to oxidative attack such as aldehyde groups should not be present and the moiety should preferably be free of unsaturation other than that of aromatic character. Preferably R^1 is a hydrocarbyl moiety.

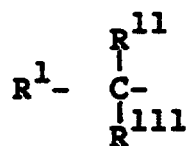
The effects of structure on the hydrophobicity of organic compounds as represented by their partition coefficients between octanol and water are described by A Leo et al in Chemical Reviews, 71, pp 525-616 (1971). The authors provide numerical values for the change in $\text{Log}P_{\text{OCT}}$ (where P_{OCT} is the partition coefficient between n-octanol and water) associated with the incorporation of various substituents into a range of structures. This permits a value for $\text{Log}P_{\text{OCT}}$ to be predicted for any structure.

All of the compounds display surface activity but this property is not very marked for compounds in which the group $\text{R}^1 - \text{C}(\text{R}^{11} \text{R}^{111}) -$ contains less than 8 carbon atoms and only those compounds in which $\text{R}^1 - \text{C}(\text{R}^{11} \text{R}^{111}) -$ contains more than 10 carbon atoms display detergent characteristics. Hydrocarbyl group branching confers increased solubility relative to linear compounds of the same number of carbon atoms and this increased solubility is associated with a decrease in surface activity relative to the corresponding linear compound. This effect also holds true for the aliphatic peroxy acids produced on perhydrolysis of the compounds. However, it has now surprisingly been found that aqueous liquors containing non linear peroxyalkanoic acids in which non linearity preferably occurs on the 2-and/or 3-carbon atoms with respect to the carbonyl carbon have a less intense odour of more aesthetically acceptable character than those containing the corresponding linear aliphatic peroxyacids. The latter characteristically have intense, pungent, and aesthetically unattractive odours which are difficult to mask using conventional detergent fragrances.

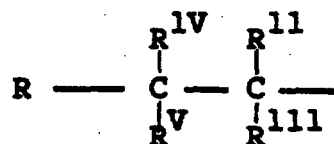
The existence of non linearity on carbon atoms further removed from the carbonyl carbon than the 3-carbon atom position also appears to be beneficial where R^1 , as hereinbefore defined comprises a cycloaliphatic or arylaliphatic moiety but is less beneficial for non cyclic aliphatic moieties where little or no odour benefit is seen for non linearity commencing at 5- or higher carbon atom positions relative to the carbonyl carbon. Accordingly, branching on 5- and higher carbon atoms where the group $R^1-C(R^{11}R^{111})-(CO)-$ is a non cyclic aliphatic acyl group is not believed to be critical to the odour forming capability of the compound. The reason for this difference in behaviour between branched and linear aliphatic peroxy acids is not well understood and does not appear to be predictable.

The introduction of non linearity into the organic group $R^1-C(R^{11}R^{111})-$ also affects the rate of perhydrolysis of the precursor in alkaline hydrogen peroxide solutions. Substitution and, in particular, di substitution of an alkyl group on the 2-carbon causes a lowering in the rate of perhydrolysis of the precursor because it hinders the approach of perhydroxyl ion and is believed to reduce the effectiveness of the percarboxylic acid as a bleach. Non linearity on the 2-carbon is thus less preferred than on the 3-carbon where e.g. di alkyl substitution has much less effect on the perhydrolysis of the compound whilst still providing an aliphatic peroxy acid of improved odour.

One preferred form of the group:

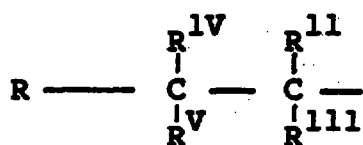


wherein R^{11} and R^{111} are as previously defined, is thus the group:



wherein

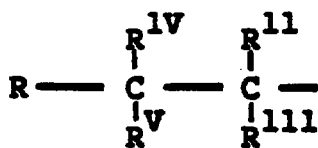
R^{1V} and R^V are each independently selected from hydrogen and C_1 - C_4 alkyl groups and the group:



comprises a C_6 - C_{16} alkyl group in which at least one of R^{11} , R^{111} , R^{1V} and R^V are C_1 - C_4 alkyl, R being an alkyl group such that there is a linear chain of five or more carbon atoms extending from and including the carbonyl carbon. Preferably R^{11} and R^{111} are hydrogen atoms.

Branched chain alkyl group-containing precursors in which there is no more than a single branch on the 2-carbon but at least one on the 3-carbon perhydrolyse at an adequate rate (i.e. 80% conversion within approximately 5 minutes) but still produce an odour when dissolved in an aqueous alkaline solution of hydrogen peroxide. However this odour is of a more acceptable type and level than that produced by the corresponding linear alkyl precursors under the same conditions.

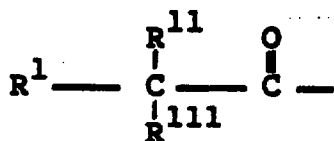
A preferred number of carbon atoms in the alkyl group:



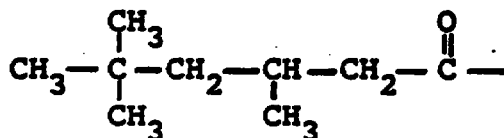
is from 7 to 9 carbon atoms with a linear chain of from 5 to 8 carbon atoms and with R_{IV} and/or R_{V} comprising a side chain i.e. in the 3-carbon position with respect to the carbonyl carbon atom.

The most preferred R group structures of this type are C_7 - C_9 radicals in which there is a single methyl side chain in the 3-carbon atom position and the alkyl group is terminated by a tertiary butyl moiety.

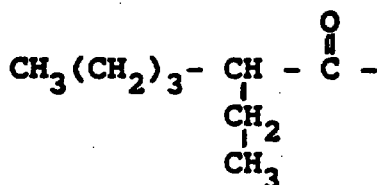
Where R_1 in the group



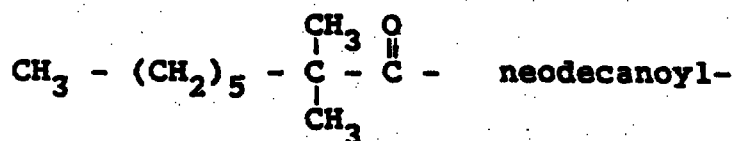
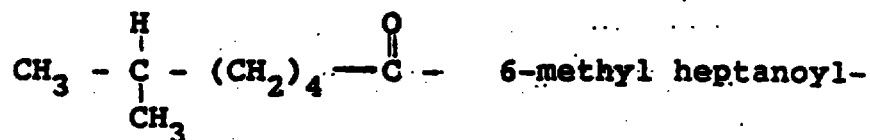
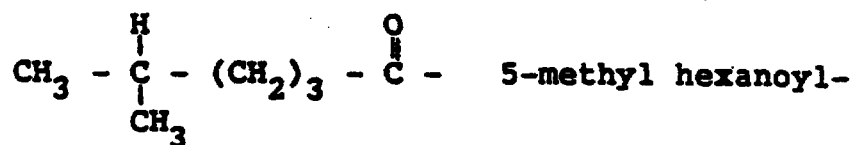
is aliphatic, structures useful for the purposes of the invention include:



3,5,5 trimethyl
hexanoyl-



2 ethyl hexanoyl-

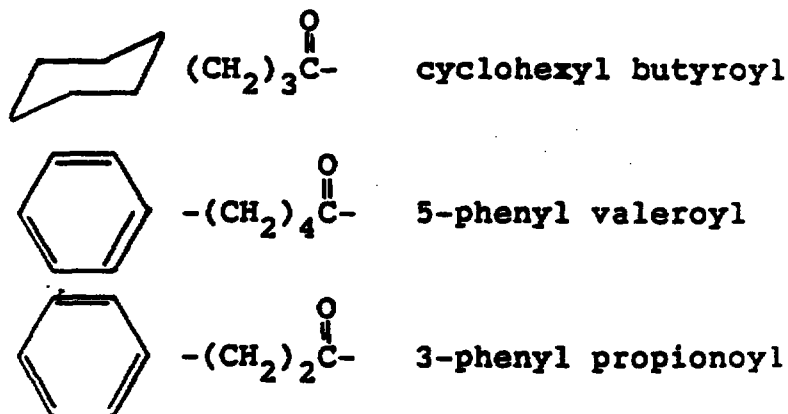


Of the above the 3,5,5 trimethyl hexanoyl structure is the most preferred for odour and rate of perhydrolysis with the 5-methyl hexanoyl 6-methylheptanoyl and neodecanoyl structures being less preferred for odour and the neodecanoyl and 2 ethyl hexanoyl structures being less preferred for the rate of perhydrolysis.

Structures useful for the purposes of the invention in which, in the group



R^1 incorporates a cyclo aliphatic or aromatic functionality include



Of the above, the 5-phenyl valeroyl and the 3-phenyl propionoyl structures are the most preferred, having a virtually bland odour and an acceptable rate of perhydrolysis.

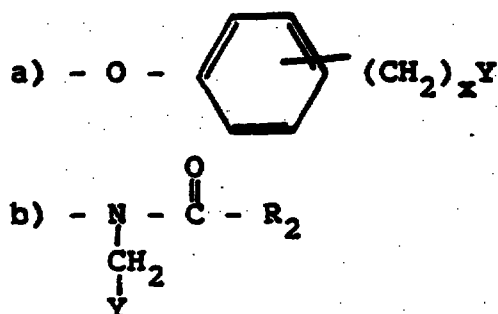
The leaving group L must be capable of displacement from the bleach precursor as a consequence of the nucleophilic attack on the bleach precursor by perhydroxyl anion generated by alkaline hydrogen peroxide. This, the perhydrolysis reaction, results in the formation of the percarboxylic acid. Generally, for a group to be a suitable leaving group it must exert an electron withdrawing effect within the precursor molecule as this facilitates the nucleophilic displacement by the perhydroxyl anion.

Suitable leaving groups for this purpose have conjugate acid forms, the pKa of which should lie within the range from 6 to 13. pKa values above 13 make the electron withdrawal effect so small as to be ineffective in promoting nucleophilic attack by perhydroxide anion, an example of such a leaving group being - OCH₃. pKa values below 6 reflect such a large electron withdrawal effect as to make the molecule reactive to a wide variety of materials including e.g. water. Certain aliphatic anhydrides fall into this class. Preferred leaving groups have a pKa in the range from 7 to 11, more preferably from 8 to 10.

However for the purposes of the present invention the leaving group must also confer a degree of solubility on the precursor molecule so that it partitions between the aqueous phase and any organic phase present. Certain leaving groups such as sulphonamide groups, having conjugate acid forms of

the appropriate pKa, do not provide sufficient aqueous solubility to the precursor molecule and therefore do not give a sufficient rate of perhydrolysis to be practicable in a laundry detergent liquor.

The leaving groups L found to be useful for the purposes of the present invention are those having the formula



wherein R_2 is an alkyl group containing from 1 to 4 carbon atoms; x is 0 or an integer from 1 to 4 and Y is selected from:

- SO_3M
- OSO_3M
- CO_2M
- $\text{N}^+(\text{R}_2)_3\text{Q}^-$
- $\text{N}(\text{R}_2)_2 \rightarrow \text{O}$

wherein M is H, alkali metal, alkaline earth metal ammonium or substituted ammonium; and Q is halide or methosulphate.

The preferred leaving group L has the formula a) in which x is 0, and Y is a sulphonate or a carboxylate, with M being sodium.

The position of the solubilising group Y on the benzene ring in formula a) is not critical in that o-, m- and p-positions provide operable species. Nevertheless polar and steric factors make the

o-substituted material most difficult to synthesise and of least value in that steric hindrance impedes the approach of perhydroxyl ion. In the preferred embodiment of leaving group L, where Y is a sulphonate radical, the precursor will normally be isolated in the form of its alkali metal salt because of the difficulty of handling the acid form.

The above mentioned precursor compounds and methods for their synthesis are described and claimed in the copending British Patent Application Publication No. 2143231.

Laundry bleaching detergent compositions are also contemplated that are adapted to form the aqueous laundry liquors of the invention incorporating the compounds, as defined above, primarily as peroxyacid bleach precursors, (the so-called low temperature bleach activators). Such detergent compositions comprise an organic surfactant, a compound as hereinbefore defined and a source of alkaline hydrogen peroxide and are normally particulate in physical form.

A wide range of surfactants can be used in the present laundry compositions. A typical listing of the classes and species of these surfactants is given in U.S.P. 3,663,961 issued to Norris on May 23, 1972.

Suitable synthetic anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates,

paraffin sulphonates, alpha-olefin sulphonates, alpha-sulpho-carboxylates and their esters, alkyl glyceryl ether sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy alkane-1-sulphonate, and beta-alkyloxy alkane sulphonate.

A particularly suitable class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts of organic sulphuric reaction products having in their molecular structure an alkyl or alkaryl group containing from 8 to 22, especially from about 10 to about 20 carbon atoms and a sulphonic acid or sulphuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups). Examples of this group of synthetic detergents which form part of the detergent compositions of the present invention are the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_{8-18}) carbon atoms produced by reducing the glycerides of tallow or coconut oil and sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from 9 to 15, especially 11 to 13, carbon atoms, in straight chain or branched chain configuration, e.g. those of the type described in U.S.P. 2,220,099 and U.S.P. 2,477,383 and those prepared from alkylbenzenes obtained by alkylation with straight chain chloroparaffins (using aluminium trichloride catalysis) or straight chain olefins (using hydrogen fluoride catalysis). Especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl group is 11.8 carbon atoms, abbreviated as $C_{11.8}$ LAS, and $C_{12}-C_{15}$ methyl branched alkyl sulphates.

Other anionic detergent compounds herein include the sodium C₁₀₋₁₈ alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulphonates and sulphates; and sodium or potassium salts of alkyl phenol polyethoxy ether sulphate containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms.

Other useful anionic detergent compounds herein include the water-soluble salts or esters of alpha-sulphonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulphonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl polyethoxy ether sulphates containing from 10 to 18, especially 12 to 16, carbon atoms in the alkyl group and from 1 to 12, especially 1 to 6, more especially 1 to 4 moles of ethylene oxide; water-soluble salts of olefin sulphonates containing from 12 to 24, preferably 14 to 16, carbon atoms, especially those made by reaction with sulphur trioxide followed by neutralization under conditions such that any sultones present are hydrolysed to the corresponding hydroxy alkane sulphonates; water-soluble salts of paraffin sulphonates containing from 8 to 14, especially from 14 to 18 carbon atoms, and beta-alkyloxy alkane sulphonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

The alkane chains of the foregoing non-soap anionic surfactants can be derived from natural

sources such as coconut oil or tallow, or can be made synthetically as for example using the Ziegler or Oxo processes. Water solubility can be achieved by using alkali metal, ammonium or alkanolammonium cations; sodium is preferred. Suitable fatty acid soaps can be selected from the ordinary alkali metal (sodium, potassium), ammonium, and alkylolammonium salts of higher fatty acids containing from 8 to 24, preferably from 10 to 22 and especially from 16 to 22 carbon atoms in the alkyl chain. Suitable fatty acids can be obtained from natural sources such as, for instance, from soybean oil, castor oil, tallow, whale and fish oils, grease, lard and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Naphthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from tallow and hydrogenated fish oil.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:5, preferably from 5:1 to 1:2, more preferably from 3:1 to 2:3. Especially preferred is a 1:1 mixture of an alkyl benzene sulphonate having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, the cation being an alkali metal, preferably sodium;

and either an alkyl sulphate having from 12 to 18, preferably from 14 to 16 carbon atoms in the alkyl radical or an ethoxy sulphate having from 10 to 20, preferably from 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of from 1 to 6, having an alkali metal cation, preferably sodium.

The nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Examples of suitable nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from 3 to 30, preferably from 5 to 14 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene and nonene. Other examples include dodecylphenol condensed with 9 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 11 moles of ethylene oxide per mole of phenol; nonylphenol and

di-isooctylphenol condensed with 13 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 24 carbon atoms, in either straight chain or branched chain configuration, with from 2 to 40 moles, preferably from 2 to 9 moles of ethylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 18 carbon atoms and is ethoxylated with between 2 and 9, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. The preferred surfactants are prepared from primary alcohols which are either linear, such as those derived from natural fats (e.g. myristyl, cetyl, stearyl alcohols), or prepared by the Ziegler process from ethylene, or partly branched such as the Lutensols, Dobanols and Neodols which have about 25% 2-methyl branching (Lutensol (RTM) being a Trade Name of BASF, Dobanol (RTM) and Neodol being Trade Names of Shell), or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic (RTM) is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants useful for the purposes of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-9, Dobanol 91-2.5, Dobanol 91-3, Dobanol 91-4, Dobanol 91-6, Dobanol 91-8, Dobanol 23-6.5, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an

average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 22 carbon atoms.

Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol (RTM) series having from 9 to 15 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

Useful nonionic surfactants also include those in which ethylene oxide is condensed with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol wherein the molecular weight of the hydrophobic portion generally falls in the range of 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic" (RTM) supplied by Wyandotte Chemicals Corporation.

Especially preferred nonionic surfactants for use herein are the C_9 - C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{12} - C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants and surfactants of a semi-polar nature, for example amine oxides. Suitable quaternary ammonium surfactants are selected from mono C_8 - C_{16} , preferably C_{10} - C_{14} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl. Suitable amine oxides are selected from mono C_8 - C_{20} , preferably C_{10} - C_{14} N-alkyl or alkenyl amine oxides and

propylene-1,3-diamine dioxides wherein the remaining N positions are again substituted by methyl, hydroxethyl or hydroxypropyl.

The detergent compositions can comprise from 1% to 70% by weight of surfactant, but usually the surfactant is present in an amount of from 1% to 20%, more preferably from 5 to 15% by weight. Mixtures of surfactant types are preferred, particularly anionic-cationic mixtures. Particularly preferred mixtures are described in British Patent No. 2040987 and European Published Patent Application No.0087914.

A source of hydrogen peroxide can be provided by any of the commercially available inorganic peroxygen bleaches and also by certain hydrogen peroxide adducts.

Suitable inorganic peroxygen bleaches include sodium perborate mono and tetra hydrate, sodium percarbonate, sodium persulfate and the clathrate $4\text{Na}_2\text{SO}_4 : 2\text{H}_2\text{O}_2 : 1\text{NaCl}$. A separate source of alkalinity is required for clathrate materials and for stability reasons this should preferably be kept physically separated from the hydrogen peroxide source by e.g. enrobing or encapsulating the latter. The hydrogen peroxide source will normally be present in an amount of from 1% to 40%, more preferably from 5% to 35% by weight of the composition and will most frequently be present in an amount of from 10% to 30% by weight.

In preferred embodiments of this aspect of the invention the levels of hydrogen peroxide source and precursor compound are arranged so that the molar ratio of hydrogen peroxide yielded by the source to precursor compound is greater than 1.5:1, normally at least 2.0. Under the usage conditions encountered in

domestic European laundry practice, this molar ratio is generally greater than 5.0:1 and most preferably is greater than 10:1.

Preferred detergent compositions, in accordance with the invention, will include those components commonly included in heavy duty laundry detergents such as suds suppressing detergent builders, chelating agents, soil suspending and anti redeposition agents, optical brightening agents, enzymes, colours and perfumes.

Suds suppressors useful in the detergent composition aspect of the invention, particularly compositions used in laundering fabrics, are represented by materials of the silicone, wax, vegetable and hydrocarbon oil and phosphate ester varieties. Suitable silicone suds controlling agents include polydimethylsiloxanes having a molecular weight in the range from 200 to 200,000 and a kinematic viscosity in the range from 20 to 2,000,000 mm²/s (cSt), preferably from 3000 to 30,000 mm²/s (cSt), and mixtures of siloxanes and hydrophobic silanated (preferably trimethylsilanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m²/g. Suitable waxes include microcrystalline waxes having a melting point in the range from 65°C to 100°C, a molecular weight in the range from 4,000-10,000, and a penetration value of at least 6, measured at 77°C by ASTM-D1321, and also paraffin waxes, synthetic waxes and natural waxes. Suitable phosphate esters include mono-and/or di-C₁₆-C₂₂ alkyl or alkenyl phosphate esters, and the corresponding mono- and/or di alkyl or alkenyl

ether phosphates containing up to 6 ethoxy groups per molecule.

Suds suppressors are normally included at levels of from 0.01% to 5% by weight of the composition, dependent on the type of suds suppressor used, more commonly 0.1% to 2% by weight.

A highly preferred component of detergent compositions in accordance with the invention is one or more detergent builder salts which may comprise up to 90% of the composition, more typically from 10% to 70% by weight thereof. Suitable detergent builder salts useful herein can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, pyrophosphates, tripolyphosphates and bicarbonates.

Examples of suitable organic alkaline detergency builder salts are water-soluble polycarboxylates such as the salts of nitrilotriacetic acid, lactic acid, glycollic acid and ether derivatives thereof as disclosed in BE -A- 821,368, 821,369 and 821,370; succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane cis, cis, cis-tetracarboxylic acid, cyclopentadiene pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic

acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexane-hexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB -A- 1,425,343.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in CA-A-755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

A further class of builder salts is the insoluble alumino silicate type which functions by cation exchange to remove polyvalent mineral hardness and heavy metal ions from solution. A preferred builder of this type has the formulation

$\text{Na}_z(\text{AlO}_2)_z(\text{SiO}_2)_y \cdot x\text{H}_2\text{O}$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5 and x is an integer from 15 to 264. Compositions incorporating builder salts of this type form the subject of GB-A-1,429,143 published March 24, 1976, DE-A-2,433,485 published February 6, 1975 and DE-A-2,525,778 published January 2, 1976.

An alkali metal, or alkaline earth metal, silicate can also be present. The amount of alkali metal silicate is preferably from 3% to 15% by weight. Suitable silicate solids have a molar ratio of $\text{SiO}_2/\text{alkali metal}_2\text{O}$ in the range from 1.0 to 3.3, more preferably from 1.5 to 2.0.

Chelating agents that can be incorporated include citric acid, nitrilotriacetic and ethylene diamine tetra acetic acids and their salts, organic phosphonate derivatives such as those disclosed in Diehl US Patent No. 3,213,030 issued 19 October, 1965; Roy US Patent No. 3,433,021 issued 14 January, 1968;

Gedge US Patent No. 3,292,121 issued 9 January, 1968; and Bersworth US Patent No. 2,599,807 issued 10 June, 1952, and carboxylic acid builder salts such as those disclosed in Diehl US Patent No. 3,308,067 issued 7 March, 1967. Preferred chelating agents include nitrilotriacetic acid (NTA), nitrilotrimethylene phosphonic acid (NTMP), ethylene diamine tetra methylene phosphonic acid (EDTMP) and diethylene triamine penta methylene phosphonic acid (DETPMP), and these are incorporated in amounts of from 0.1% to 3%, more preferably 0.2% to 2% by weight of the composition.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Preferred polymers include copolymers or salts thereof of maleic anhydride with ethylene, methylvinyl ether, acrylic acid or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These polymers are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Enzymes suitable for use herein include those discussed in U.S.P. 3,519,570 and U.S.P. 3,533,139 to McCarty and McCarty et al issued July 7, 1970 and

January 5, 1971, respectively. Photoactivators are discussed in EP-A-57088, highly preferred materials being zinc phthalocyanine tri- and tetra-sulphonates.

Anionic or nonionic optical brighteners are also preferred ingredients of detergent compositions in accordance with the invention, being normally present at levels of from 0.01% to 1% by weight, more preferably at levels of from 0.02% to 0.5% by weight.

Anionic fluorescent brightening agents are well-known materials, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2'-disulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2'-disulphonate, disodium 4,4'-bis(2'-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'-disulphonate, sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3-triazole-2''-sulphonate and di-sodium 4,4'-bis(2-sulphonato styryl) biphenyl.

Other fluorescers to which the invention can be applied include the 1,3-diaryl pyrazolines and 7-alkylaminocoumarins.

A preferred fluorescer is the anionic material available from Ciba Geigy S.A. under the trade name Tinopal CBS(RTM) and mixtures thereof with materials available under the trade names Tinopal EMS and

Blankophor MBBN(RTM), the latter being sold by Farbenfabriken Bayer AG.

The non-linear peroxyalkanoic acid precursors are normally used at levels of from 1% to 15% by weight more preferably at from 1% to 10% and most frequently at from 2% to 5% by weight of the detergent composition. They can be incorporated into a detergent composition in a number of ways, most if not all of which are intended to minimise any reaction between the precursor and other components during storage prior to use.

Thus the precursor may be formed into particulates by spray cooling, prilling, marumerising, agglomeration or granulation, either alone or together with a carrier material which may be organic or inorganic in type. Suitable inorganic materials include clays and other natural and synthetic aluminosilicates, as well as hydratable salts such as phosphates, carbonates and sulphates. Suitable organic materials include ethoxylated C_{12} - C_{18} alcohols and alkyl phenols, polyethylene glycols of MWT 4,000-10,000, C_{12} - C_{18} fatty acids and esters thereof with monohydric and polyhydric alcohols. In one preferred method of manufacturing the precursor, disclosed in Published European Patent Application No. 0105672, filed September 22 1983, the liquid reaction product containing the precursor is blended with the carrier material under an inert gas atmosphere before being processed further to form the particulate material to be added to the detergent. This technique is particularly suitable when the carrier is a waxy organic solid such as an ethoxylated alcohol

or ester and a highly preferred example, employing a glycerol mono C₁₀-C₁₄ fatty acid ester carrier is disclosed in the Applicants' Published European Application No. 0123423.

In another method of manufacturing the preferred alkali metal C₇-C₉ branched chain acyl oxybenzene sulphonate phenol sulphonate precursors, one of the reaction components e.g. alkali metal phenol sulphonate or fatty acid is employed in a greater excess than is necessary to achieve the desired completeness of reaction. The excess reactant is used as a binder material for the reaction product which is taken from the reactor and, without separate crystallisation or solvent extraction steps, is compacted to form particulates which can be added directly to the detergent composition.

Preferred methods of making a particulate from a mixture of precursor and an organic carrier or builder are disclosed in the Applicants' Published European Application Nos. 62523 and 0106634.

Particulates incorporating non linear substituted or unsubstituted peroxyalkanoic acid precursors useful in the present invention are normally added to the spray dried portion of the detergent composition with the other dry-mix ingredients such as enzymes, inorganic peroxygen bleaches and suds suppressors. It will be appreciated however that the detergent composition to which the precursor particulates are added may itself be made in a variety of ways such as dry-mixing, agglomeration extrusion, flaking etc, such ways being well known to those skilled in the art and not forming part of the present invention.

A further aspect of the invention relates to

detergent additive products suitable for forming aqueous laundry bleaching liquors and incorporating non linear peroxyalkanoic acid precursors whose alkanoic acid analogues have a $\log P_{OCT}$ of from 1.9 to 4.1. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and may contain any of the components of such compositions, although they will not comprise all of the components present in a fully formulated detergent composition. Additive products in accordance with this aspect of the invention will normally be added to an aqueous liquor containing a source of (alkaline) hydrogen peroxide, although under certain circumstances a source of alkaline hydrogen peroxide may be included in the product.

Additive products in accordance with this aspect of the present invention may comprise the precursor alone in combination with a carrier such as a compatible particulate substrate, a flexible non particulate substrate or a container. Examples of compatible particulate substrates include inert materials such as clays and other aluminosilicates including zeolites both natural and synthetic in origin. Other compatible particulate carrier materials include hydratable inorganic salts such as phosphates, carbonates and sulphates.

Additive products enclosed in bags or containers are manufactured such that the containers prevent egress of their contents when dry but are adapted to release their contents on immersion in an aqueous solution.

A convenient execution of this form of the additive product comprises a particulate solid

non linear peroxyalkanoic acid precursor enclosed in a container. Usually the container will be flexible, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European Published Patent Application No. 0018678. Alternatively it may be formed of a water insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European Published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

An alternative form of the additive product comprises a non linear peroxyalkanoic acid precursor in water releasable combination with a non particulate flexible substrate in a weight ratio of 1:10 to 30:1. Additive products of this type are disclosed in British Patent Specification Nos. 1,586,769 and 2040983B and also in British Published Patent Application No. 2125453.

The substrate may itself be water soluble or water insoluble and in the latter case it should possess sufficient structural integrity under the conditions of the wash to be recovered from the machine at the end of the laundry cycle. Structures which are water disintegratable i.e. that break down in aqueous media to insoluble individual fibres or particles are considered less satisfactory for the purposes of the present invention.

Water soluble materials include certain cellulose ethers, alginates, polyvinyl alcohol and water soluble polyvinyl pyrrolidone polymers, which can be formed into non-woven and woven fibrous structures. Suitable water insoluble materials include, but are not restricted to, natural and synthetic fibres, foams, sponges and films.

The substrate may have any one of a number of physical forms such as sheets, blocks, rings, balls, rods or tubes. Such forms should be amenable to unit usage by the consumer, i.e. they should be capable of addition to the washing liquor in measured amounts, such as individual sheets, blocks or balls and unit lengths of rods or tubes. Certain of these substrate types can also be adapted for single or multiple uses, and can be provided with loadings of organic peroxy acid precursor up to a precursor:substrate ratio of 30:1 by weight.

One such article comprises a sponge material releasably enclosing enough organic peroxy compound precursor to provide bleaching action during several washing cycles. This multi-use article can be made by impregnating a sponge ball or block with about 20 grams of the precursor and any adjuncts therewith. In use, the precursor leaches out through the pores of the sponge into the wash liquor and reacts with the inorganic peroxy bleach. Such a filled sponge can be used to treat several loads of fabrics in conventional washing machines, and has the advantage that it can remain in the washer after use.

A highly preferred execution of this type of additive product utilises a flexible sheet so as to make it compatible with the movement of the fabrics in

the washing machine and to facilitate its handling during manufacture of the product. Preferably the sheet is water pervious i.e. water can pass from one surface of the sheet to the opposite surface and, for film type substrates, perforation of the sheet is desirable. The most preferred form of the substrate is a sheet of woven or non-woven fabric or a thin sheet of cellular plastics material. Woven fabric sheets can take the form of a plain weave natural or synthetic fibre of low fibre count/unit length, such as is used for surgical dressings, or of the type known as cheese cloth. Loading limitations on sheet type substrates limit the amount of precursor compound that can be applied to the sheet and, in practice, the weight ratio of precursor compound:sheet substrate normally lies within the range from 1:2 to 10:1.

Variations on the above sheet substrate product forms are also contemplated for the purposes of the present invention. For example, laminated sheet products can be employed in which a central layer is impregnated and/or coated with a composition incorporating the bleach precursor and then one or more outer layers are applied to produce a fabric-like aesthetic effect. The layers may be sealed together so as to remain attached during use or may separate on contact with water to facilitate the release of the coated or impregnated material.

An alternative laminate form comprises one layer embossed or deformed to provide a series of pouch-like containers into each of which the bleach precursor and optionally other detergent components are deposited in measured amounts, with a second layer overlying the first layer and sealed thereto in those areas between

the pouch-like containers where the two layers are in contact. The bleach precursor and any accompanying components may be deposited in particulate, paste or molten form and the laminate layers should prevent egress of the contents of the pouch-like containers prior to their addition to water. The layers may separate or may remain attached together on contact with water, the only requirement being that the structure should permit rapid release of the contents of the pouch-like containers into solution. The number of pouch-like containers per unit area of substrate is a matter of choice but will normally vary between 500 and 25,000 per square metre.

As stated above, suitable materials which can be used as a substrate in the invention herein include, among others, sponges, paper, and woven and non-woven fabrics.

A suitable sponge like material that can be used in the present invention comprises an absorbent foam like material in the form of a sheet. The term 'absorbent foam-like material' is intended to encompass three dimensional absorptive materials such as 'gas blown foams', natural sponges and composite fibrous based structures such as are disclosed in US Patent Nos. 3311115 and 3430630. A particularly suitable material of this type is a hydrophilic polyurethane foam in which the internal cellular walls of the foam have been broken by reticulation. Foams of this type are described in detail in Dulle US Patent No. 3794029. A preferred example of this foam type comprises a hydrophilic polyurethane foam of density 0.596 grs per cubic inch with a cell count of between 8 and 40 cells per cm, preferably about 24 to

32 per cm available from the Scott Paper Company, Eddystone, Pennsylvania USA., under the Registered Trade Mark "Hydrofoam". Preferred sheets of this type of material have thicknesses in the range from 3 to 5 mm.

Preferred sheet substrates for use in this type of additive product are apertured and non apertured non woven fabrics which can generally be defined as adhesively bonded fibrous or filamentous products, having a web or carded fibre structure (where the fibre strength is suitable to allow carding) or comprising fibrous mats, in which the fibres or filaments are distributed haphazardly or in random array (i.e. an array of fibres in a carded web wherein partial orientation of the fibres is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibres or filaments can be natural (e.g. wool, silk, wood pulp, jute, hemp, cotton, linen, sisal, or ramie), synthetic (e.g. rayon, cellulose, ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters) or mixtures of any of the above.

The choice of binder-resins used in the manufacture of non-woven cloths can provide substrates possessing a variety of desirable traits. For example, the absorbent capacity of the cloth can be increased, decreased, or regulated by respectively using a hydrophilic binder-resin, a hydrophobic binder-resin or a mixture thereof in the fibre bonding step. Moreover, the hydrophobic binder-resin, when used singly or as the predominant compound of a hydrophobic-hydrophilic mixture, provides non-woven cloths which are especially useful as substrates when

the precursor-substrate combinations disclosed herein are used in an automatic washer.

When the substrate herein is a bonded non-woven cloth made from fibres, deposited haphazardly or in random array on the screen, the compositions exhibit excellent strength in all directions and are not prone to tear or separate when used in the washer.

Preferably, the non-woven cloth is water-laid or air-laid and is made from cellulosic fibres, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant. Preferably the fibres are from 4 to 50 mm in length and are from 1.5 to 5 denier (Denier is an internationally recognised unit in yarn measure, corresponding to the weight in grams of a 9,000 meter length of yarn). Preferably the fibres are at least partially orientated haphazardly, particularly substantially haphazardly, and are adhesively bonded together with hydrophobic or substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. Conveniently, the cloth comprises 70% fibre and 30% binder-resin polymer by weight and has a basis weight of from 10 to 100, preferably from 24 to 72 g/m².

Apertured non-woven substrates are also useful for the purposes of the present invention. The apertures, which extend between opposite surfaces of the substrate are normally in a pattern and are formed during lay-down of the fibres to produce the substrate. Exemplary apertured non-woven substrates are disclosed in US Patent Nos. 3,741,724, 3,930,086 and 3,750,237.

A suitable diamond patterned apertured substrate

is obtainable from Chicopee Manufacturing Co., Milltown, New Jersey, USA under the Code No. SK 650 WFX 577 and comprising a polyester-wood pulp mixture having a basis weight of 50 g/m^2 and approximately 13 apertures per square cm.

Another preferred example of an apertured non-woven substrate, also available from Chicopee Manufacturing Co., under the Code No. AK 30 ML 1379 comprises a regenerated cellulose sheet of 3.0 denier fibres bonded with Rhoplex RA 8 binder (fibre:binder ratio 70:30) having a basis weight of 40 g/m^2 and 17 apertures/cm². A highly preferred square patterned apertured substrate of similar composition but fibre:binder ratio of 80:20 and basis weight 35 g/m^2 is also available from Chicopee BV Holland.

In general, apertured fabrics for the purposes of the invention have from 10-20 apertures/cm², preferably 12-18 apertures/cm².

The size and shape of the substrate sheet is a matter of choice and is determined principally by factors associated with the convenience of its use. Thus the sheet should not be so small as to become trapped in the crevices of the machine or the clothes being washed or so large as to be awkward to package and dispense from the container in which it is sold. For the purposes of the present invention sheets ranging in plan area from 130 cm^2 to 1300 cm^2 are acceptable, the preferred area lying in the range of from 520 cm^2 to 780 cm^2 .

Additive products in particulate substrate form can comprise powders, flakes, chips, tablets or noodles which may be used as-is or may themselves be enclosed in containers for addition to an aqueous

liquor.

More usually, additive products in accordance with the invention contain other detergent ingredients in addition to the hereinbefore defined compounds.

The type and level of such optional materials is constrained only by the requirements of unreactivity towards the precursor, and, where a substrate is utilised as the, or a carrier, by the loading limitations of the substrate. This imposes a maximum weight ratio of optional ingredients to substrate of about 10:1, and in the case of coated sheet substrates of about 8:1. As described in more detail hereinafter, materials that are capable of reaction with the precursor can be incorporated in additive products of the present invention but it is essential that the precursor is spatially separate therefrom, i.e. is disposed at a substrate location that is free or substantially free of the other reactant materials..

One factor determining the acceptable level of incorporation of an optional ingredient is its physical characteristics i.e. whether it is liquid or solid and if solid whether it is crystalline or waxy and of high or low melting or softening point.

Highly desirable optional components are solid, water soluble or water dispersible organic processing aids of a waxy nature having a Mpt in the range 30-80°C. The most preferred processing aids have a softening point greater than 40°C and a melting point less than 80°C to permit their easy processing.

The preferred processing aids serve as plasticisers or thickeners in the incorporation of the precursors into or onto the substrate and ideally are non-hygroscopic solids that are mixed with the

precursors and melted to provide mixtures having a viscosity of up to 30,000 centipoises at 50°C.

Typical solids are C₁₄-C₁₈ primary and secondary alcohols and C₁₂-C₂₀ fatty acids and ethoxylates thereof containing from 15 to 80 ethylene oxide groups per mole of alcohol, sorbitan esters of C₁₂-C₂₀ fatty acids and polyethylene glycols of Mwt 4,000-10,000. As stated hereinbefore, preferred materials are those of low hygroscopicity particularly the C₁₄-C₁₈ saturated fatty acids.

The C₁₆-C₁₈ fatty acids and polyethylene glycols of Mwt 4,000-8,000, are particularly effective when used in amounts such that the weight ratio of bleach precursor:processing aid lies in the range 20:1 to 1:2 particularly 4:1 to 1:1.

In addition to the foregoing optional components that are of primary value in incorporating the precursor onto, and releasing it from, the substrate, conventional detergent ingredients can be incorporated into the composition provided that they are not reactive towards the non linear peroxyalkanoic acid precursor. Thus, surfactants, suds modifiers, chelating agents, anti-redeposition and soil suspending agents, optical brighteners, bactericides, anti-tarnish agents, enzymatic materials, fabric softeners, antistatic agents, perfumes and bleach catalysts can all be introduced into the wash liquors of the present invention by means of additive products, subject to the constraints imposed by the loading limitations of the substrate.

In detergent additive products in which the compositions comprise a non linear peroxyalkanoic acid precursor disposed on a substrate of either particulate or non particulate form, the substrate is preferably absorbent and the composition is impregnated therein.

Application of the precursor can be carried out in any convenient manner, and many methods are known in the art. As the preferred acyloxybenzene sulphonate or carboxylate precursors are solid at temperatures in excess of 150°C, one form of application is by solution in organic solvents which are volatilised after application, whilst another employs a slurry or suspension of the finely divided solid in water or other liquid media.

Preferred compositions in accordance with the invention are substantially anhydrous and thus incorporation on the substrate is best accomplished by utilisation of a non aqueous liquid medium.

A highly preferred embodiment of this aspect of the invention utilises a processing aid and/or other optional ingredients in molten form as the liquid medium in which the finely divided precursor is dispersed.

Where the substrate comprises a non-sheet like reticulated foam article, direct impregnation of the article by a liquid medium incorporating the dispersed precursor, either alone or with other components of the formulation can be used, employing methods known in the art and described in more detail hereinafter. Where the substrate comprises a non-woven material or a foam article of sheet-like form, it is preferred to mix the bleach precursor with a compatible non-hygroscopic material of melting point 80°C, such as the processing aids hereinbefore described to provide a waxy solid in which the bleach precursor is

present in the form of a solid solution and/or as a dispersed phase. The melting point range and waxy nature of polyethylene glycols of molecular weight 4000 makes them useful for this purpose.

Where nonionic surfactants form components of the composition, their physical properties may permit their use as, or as part of, a liquid medium in which the precursor and other solid components are incorporated.

As previously indicated, materials reactive towards the peroxy bleach precursor compounds useful in the invention can be incorporated in detergent additive products containing them provided that the precursor and the reactive material are spatially separated from one another. Inorganic peroxygen bleaches which either contain water or hydrogen peroxide in hydrogen bonded form, such as sodium perborate monohydrate and tetrahydrate, sodium percarbonate, sodium persulfate or sodium perpyrophosphate, and also urea-hydrogen peroxide addition products, are materials which are sufficiently reactive to require this spatial separation.

Where the precursor and the inorganic peroxygen bleach are incorporated in physically separate locations on the same non particulate sheet substrate, a convenient method of application is the deposition of the respective melts, suspensions or solutions as discrete bands of material on the substrate. This can be achieved using a divided extrusion head or by applying the melt or suspension to separate webs of substrate which are subsequently joined longitudinally. Preferably the bleach is applied as

a dispersion of solid particles in a molten processing aid (as hereinbefore described) at a temperature in the range 40° and 60°C. Using this technique, bleach:substrate weight ratios of up to 15:1 can be obtained. This level of loading is attainable with cellular substrates but substrates of fibrous character tend to be limited in practice to bleach:substrate weight ratios of no more than 8:1. Furthermore, loading limitations imposed by the substrate surface area required for the incorporation of the precursor may limit the amount of bleach to less than this and bleach:substrate weight ratios in the range 5:1 to 1:2 are normally employed. Provision must also be made for the separation of the bands or areas of bleach and the corresponding bands or areas of precursor during transport and/or storage. This is achieved by interposing layers of material between the layers of substrate or by producing patterns of deposited material that are not coincident on stacking of the substrate.

A preferred method of making the particulate substrate forms of detergent additive product is by applying a spray of the composition as a solution dispersion or molten suspension on to a moving bed of particulate substrate in a rotating drum or pan fluidised bed, or a rotating blade mixer of the Schugi (RTM) or Patterson-Kelly type.

In a preferred method of making sheet substrate additive products useful in the invention, the precursor(s), dissolved or dispersed in a molten processing aid, are held in a trough formed by the nip of two horizontal rolls arranged side by side and rotating in opposite directions such that the nip is

formed by surfaces having approximately the same velocity in a downward direction. Molten material is spread on one of the rolls and transferred to a continuous web of substrate whose speed is the same as that of the roll and which contacts the roll over a limited length of its periphery. The impregnated substrate is then contacted by a smoothing and spreading roll having a direction of rotation such that its contact surface is moving in the opposite direction to that of the substrate. The rolls employed in this technique are fabricated in metal and are heated to maintain the impregnating mixture in the liquid phase.

A further aspect of the present invention comprises a bleaching composition adapted to form an aqueous laundry bleaching liquor and composed of a non linear peroxyalkanoic acid precursor in combination with a source of hydrogen peroxide in the form of an alkali metal inorganic peroxy salt or a hydrogen peroxide clathrate.

In a composition comprising a mixture of the precursor and a source of alkaline hydrogen peroxide it is very desirable that the two components be isolated from each other in order that a reaction does not occur prior to use. Although a reaction can be prevented by making an anhydrous mixture of the two components, the maintenance of such a mixture in the anhydrous state is very difficult under normal storage conditions. A preferable technique is to separate the components physically, by coating one or both with inert materials that dissolve or disperse in aqueous media, by incorporating each in separate or compartmental packaging, or by fixing each component to separate locations on a non particulate

substrate. Each of these separation techniques is well known in the art and does not form part of the present invention.

Bleaching compositions of this type contain from 30% to 95% by weight of the hydrogen peroxide source and 70% to 5% by weight of the precursor compound as hereinbefore defined; more generally from 50% to 90% of hydrogen peroxide source and from 50% to 10% of precursor compound, most preferably from 75% to 90% of hydrogen peroxide source and from 25% to 10% of precursor compound.

In addition to the non linear peroxyalkanoic acid precursor compounds as described hereinbefore, products and compositions useful in forming the laundry bleaching liquors of the present invention may optionally contain any of the organic peroxy bleach precursors known in the art. A detailed disclosure of such precursors is provided in British Patent Specification No. 2040983. For the purposes of the present invention, blends of branched C_8-C_{10} acyl oxybenzene sulphonate or carboxylate with peracetic acid precursors are preferred, examples of such peracetic acid precursors including tetra acetyl ethylene diamine, tetra acetyl methylene diamine, tetra acetyl glycouril, sodium p-acetoxybenzene sulphonate, penta acetyl glucose, octa acetyl lactose. However, the invention also contemplates blends of branched C_8-C_{10} carbon chain-containing precursors with e.g. peroxybenzoic and peroxyphthalic acid precursors where different combinations of bleaching properties are required.

In blends of the preferred branched C_8-C_{10} acyl oxybenzene sulphonate precursors with other peroxyacid precursors it has been found that the C_8-C_{10} acyl oxybenzene sulphonate should

preferably be present in an amount to provide a level of at least 2 ppm and preferably at least 5 ppm available oxygen in the wash liquor, in order that the benefit of the C₈-C₁₀ peroxy acid can be realised. Generally the weight ratio of the branched C₈-C₁₀ acyl oxybenzene sulphonate precursor to the other peroxy acid (e.g. peracetic acid) precursor should be such as to provide a non linear C₈-C₁₀ peroxyalkanoic acid:peracetic acid molar ratio in the range from 3:1 to 1:5 preferably from 2:1 to 1:3 most preferably from 1.8:1 to 1:2. Under European washing conditions, blends in which the branched C₈-C₁₀ acyl oxybenzene sulphonate delivers from 5-15 ppm available oxygen in the wash liquor are preferred.

The level of usage of the precursor will naturally be dependent on a number of factors e.g. the size of the fabric load in the machine, the level of bleaching performance desired, the amount of perhydroxyl ion in the wash solution, the bleaching efficacy of the organic peroxy species derived from the precursor and the efficiency of conversion of the precursor into that peroxy species. It is conventional with inorganic peroxy bleaches to provide a level of available oxygen in solution from 50 ppm to 350 ppm by weight for heavy duty laundry purposes. However, when using organic peroxy bleaches a level of available oxygen provided by the organic peroxy compound may lie in the range from 1 ppm to 50 ppm, levels of from 1.5 ppm to 16 ppm being appropriate under conventional US washing conditions while levels of from 20 ppm to 50 ppm are more commonly used under European washing conditions. This level of available oxygen should be attained within the normal wash cycle

time i.e. within 5-15 minutes depending on the particular wash cycle being employed.

For a machine having a liquid capacity in use of 20 to 30 litres, such a level of available oxygen requires the delivery of from 1 gr to 20 gr of organic peroxy compound precursor assuming quantitative conversion.

Various aspects of the invention are illustrated in the following Examples in which all parts and percentages are by weight unless otherwise specified.

C ₁₂ LAS	: Sodium linear C ₁₂ alkyl benzene sulphonate
C ₁₃ LAS	: Sodium linear C ₁₃ alkyl benzene sulphonate
ASC	: Disodium salt of α -sulphonated stearic acid
TAS	: Sodium tallow alcohol sulphate
C _{14/15} AS	: Sodium C ₁₄ -C ₁₅ alkyl sulphate
C _{12/14} AS	: Sodium C ₁₂ -C ₁₄ alkyl sulphate
TAE _n	: Tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
C ₁₄ TMAB	: C ₁₄ alkyl trimethyl ammonium bromide
C ₁₄ TMAMS	: C ₁₄ alkyl trimethyl ammonium methyl sulphate
C ₁₂ TMAB	: C ₁₂ alkyl trimethyl ammonium bromide
A 45E7	: A C ₁₄₋₁₅ primary alcohol condensed with 7 moles of ethylene oxide.

A 23 E6.5	: A C ₁₂ -C ₁₃ primary alcohol condensed with 6.5 moles of ethylene oxide.
Soap	: Sodium salt of 80/20 mixture of tallow and coconut fatty acids.
PEG	: Polyethylene glycol (Mwt normally follows)
TAED	: Tetraacetyl ethylene diamine
PAG	: Penta acetyl glucose
AOBS	: Sodium p-acetoxy benzene sulphonate
ISONOBS	: Sodium 3,5,5 trimethyl hexanoyl oxybenzene sulphonate
ISONOBA	: Sodium 3,5,5 trimethyl hexanoyl oxybenzoic acid
EHOBS	: Sodium 2-ethyl hexanoyl oxybenzene sulphonate
Silicate	: Sodium silicate having an SiO :Na O ratio of 1.6 2 2
Sulphate	: Anhydrous sodium sulphate
STP	: Sodium tripolyphosphate
Zeolite A	: Sodium aluminosilicate of formula Na ₁₂ (AlO ₂ .SiO ₂) ₁₂ 27H ₂ O.
Carbonate	: Anhydrous sodium carbonate
CMC	: Sodium carboxymethyl cellulose
Silicone Compound	: 85% polydimethyl siloxane 15% silica
Silicone Prill	: Comprising 0.14 parts by weight of an 85:15 by weight mixture of silanated silica and silicone, granulated with 1.3 parts of sodium tripolyphosphate, and 0.56 parts of tallow alcohol condensed with 80 molar proportions of ethylene oxide

MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000.
MVEMA	: Maleic anhydride/vinyl methyl ether copolymer, believed to have an average molecular weight of 240,000. This material was prehydrolysed with NaOH before addition.
Perborate	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
Perborate monohydrate	: Anhydrous sodium perborate bleach of empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Enzyme	: Mixed proteolytic and amylolytic enzyme sold by Novo Industrie AS.
EDTA	: Sodium ethylene diamine tetra acetate
NTA	: Sodium nitrilotriacetate.
Brightener 1	: Disodium 4,4'-bis (2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene-2:2'-disulphonate.
Brightener 2	: Disodium 4,4'-bis(2-sulphonato styryl)biphenyl
DETPMP	: Diethylene triamine penta(methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest (RTM) 2060.
EDTMP	: Ethylenediamine tetra (methylene phosphonic acid), marketed by Monsanto, under the Trade name Dequest 2041.

H_2O_2 Clathrate : A clathrate of $4Na_2SO_4$:
 $2H_2O_2$: $1NaCl$
Mixed Suds : 25% paraffin wax Mpt $50^{\circ}C$, 17%
Suppressor hydrophobic silica, 58% paraffin
oil.

EXAMPLES 1-6

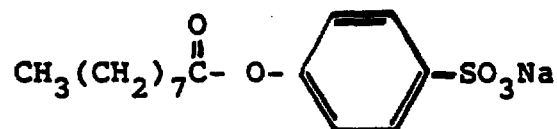
Detergent compositions incorporating ISONOBS as the peroxy acid precursor have the following percentage formulations:

	1	2	3	4	5	6
C ₁₂ LAS	-	6.0	4.7	-	-	6.0
C ₁₃ LAS	4.0	-	-	9.0	8.0	-
C _{14/15} AS	8.0	6.0	7.0	3.0	-	6.0
A4527	-	2.0	2.1	2.5	-	2.0
C ₁₄ TMAB	2.0	2.0	2.1	-	1.5	2.0
C ₁₂ TMAB	-	-	-	1.5	-	-
STP	24.0	24.0	18.0	32.0	24.0	12.0
MA/AA	1.5	1.7	-	-	1.5	3.0
MVEMA	-	-	1.0	0.5	0.5	-
Silicate	10.0	5.0	7.5	5.0	7.5	5.0
Carbonate	5.0	10.0	5.0	-	2.5	10.0
EDTMP	0.25	0.3	0.1	0.1	0.1	0.2
Perborate	18.0	21.0	24.0	24.0	18.0	21.0
Peroxy acid precursor	3.0	3.0	5.0	3.0	3.0	8.5
Silicone Prill	3.0	4.0	4.0	2.5	2.0	4.0
Brightener 1	0.25	0.25	0.20	0.25	0.25	0.20
Enzyme	0.4	0.3	0.4	0.25	0.30	0.30
Sulphate	9.0	5.0	12.0	6.4	15.35	15.0
Moisture + Misc.	-----To 100-----					

Typically a spray dried base powder is made containing the anionic and cationic surfactants, STP, inorganic salts, brightener, copolymer and EDTMP and then the remaining ingredients are incorporated by spray on to the base powder nonionic, dry mixing (perborate) or via prill addition (peroxy acid

precursor, silicone and enzyme).

An additional comparative formulation 2A was made up in accordance with Example 2 except that the peroxy acid precursor had the structural formula



Formulations 2 and 2A were each made up into a 0.2% by weight aqueous solution at 60°C, and both formulations displayed a rate of perhydrolysis that was > 95% complete after 2 minutes. However, whilst formulation 2A had a strong bleachy odour, formulation 2 was virtually odourless. Application of perfume by spray-on to both formulations prior to making up the aqueous solutions did not mask the solution odour of formulation 2A, whilst providing the expected pleasant odour to the solution of formulation 2.

EXAMPLES 7-12

The following formulations represent examples of the detergent composition aspect of the invention.

	7	8	9	10	11	12
LAS	8.0	8.0	8.0	-	7.0	5.0
C _{14/15} AS	4.0	-	-	9.0	-	3.0
TAS	-	-	4.0	3.0	-	-
C _{12/14} AS	-	-	-	-	2.0	-
C ₁₂ TMAB	-	2.0	2.0	-	2.0	-
Dobanol 45-E-7	4.0	6.0	5.0	6.0	5.0	10.0
TAE ₁₁	-	0.5	-	-	2.0	-
TAED	0.5	-	6.0	-	-	-
Silicate	5.0	6.0	3.0	7.0	4.0	10.0
Mixed Suds						
Suppressor	2.0	2.0	-	2.0	-	2.0
Silicone Prill	-	-	2.0	3.0	-	0.5
MVEMA	-	-	0.8	1.5	-	1.0
MA/AA	2.0	1.0	-	-	1.2	-
Brightener 1	0.3	0.2	0.4	0.3	0.2	0.2
DETMP	0.3	-	-	-	-	0.2
EDTMP	-	-	0.4	-	-	-
Sodium Perborate	12.0	15.0	16.0	18.0	10.0	15.0
Enzyme	0.6	1.0	-	-	-	0.8
Sodium						
Tripolyphosphate	30.0	28.0	25.0	32.0	28.0	30.0
Magnesium						
Sulphate	-	0.5	-	-	-	0.5
ISONOBS	2.5	4.0	-	-	3.0	-
EHOBS	-	-	2.0	-	-	5.0
ISONOBA	-	-	1.5	6	-	-

Sodium Sulphate,

Moisture

-----To 100-----

and Miscellaneous

EXAMPLES 13-18

Laundry additive products incorporating precursor compounds in water releasable combination with a sheet substrate are prepared having the compositions shown below in parts by weight:

	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
ISONOBS	7.6	5.2	10.5	8.4	4.2	5.2
PAG	-	-	-	2.5	4.0	-
TAED	-	3.6	-	-	-	-
AOBS	-	-	-	-	-	3.0
A45E7	5.0	5.0	5.0	5.0	5.0	5.0
PEG 8000	5.0	7.0	8.0	8.0	6.0	6.0
C ₁₄ TMAB	-	2.0	-	-	2.0	-
C ₁₄ TMAMS	-	-	-	2.0	-	2.0
EDTMP	0.5	0.5	0.5	0.5	0.5	0.5
MVEMA	0.3	0.3	0.3	0.3	0.3	0.3
Silicone Compound	0.25	0.25	0.25	0.25	0.25	0.25
Brightener 2	0.1	0.1	0.1	0.1	0.1	0.1
Perfume	0.1	0.1	0.1	0.1	0.1	0.1
Substrate	2.8	2.8	2.8	2.8	2.8	2.8

The substrate in each instance is a square patterned apertured non-woven sheet, of size 23 x 35 cm and basis weight 2.8 g, formed of 100% unbleached crimped rayon fibres (80% fibre, 20% polyacrylate binder). In the case of Examples 13 and 15 the products are made by forming a melt of the PEG and A45E7 at approximately 80°C, dispersing the other components (except the perfume) therein and applying the resultant slurry to the substrate from an

applicator roll with which the substrate is brought into contact. Additional rolls are used to spread the slurry before it is cooled to ambient temperature to solidify the composition. Perfume is then sprayed on to the impregnated substrate to produce the final product.

Examples 14 and 16-18 use a similar procedure except that the product is applied to the sheet via a divided extruder head instead of an applicator roll, the division permitting the cationic surfactant, together with 1.0 part of A45E7 and 2.0 parts of PEG 8000 from the formulation to be applied as a separate stripe.

EXAMPLES 19-23

The following formulations are further detergent compositions in accordance with the invention.

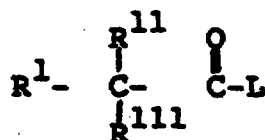
	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>
LAS	4.0	8.0	-	7.0	-
C _{14/15} AS	4.0	-	-	-	-
TAS	-	4.0	-	2	-
ASC	-	-	15.0	-	20.0
Soap	-	2.0	10.0	-	25.0
Dobanol 45-E-7	4.0	5.0	6.0	5.0	10.0
TAED	1.0	1.0	-	1.0	-
Silicate	5.0	3.0	7.0	4.0	10.0
Mixed Suds					
Suppressor	2.0	-	-	-	2.0
Silicone Prill	-	2.0	3.0	-	0.5
MVEMA	-	0.8	1.5	-	1.0
NTA	-	2.5	-	2.5	5.0
Brightener 1	0.3	0.4	0.3	0.2	0.2
DETPMP	-	-	-	-	0.2
EDTMP	1.0	-	-	1.0	-
Sodium Perborate	12.0	16.0	18.0	10.0	15.0
Enzyme	0.6	-	-	-	0.8
Zeolite A	30.0	25.0	-	10.0	-
Carbonate	10.0	5.0	15.0	20.0	-
Sodium citrate	-	-	10.0	-	5.0
ISONOBS	3.0	4.0	-	3.0	-
EHOBS	-	-	-	-	5.0
ISONOBA	-	-	6.0	-	-

Sodium Sulphate,
Moisture and
Miscellaneous

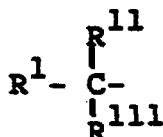
-----To 100-----

**CLAIMS**

1. An aqueous laundry bleaching liquor having a bland odour comprising a source of alkaline hydrogen peroxide in an amount to give a level of available oxygen of from 50 to 350 ppm together with a non-linear substituted or unsubstituted peroxyalkanoic acid precursor in an amount to give from 1 to 50 ppm of available oxygen from the peroxyalkanoic acid upon reaction with said alkaline hydrogen peroxide source, said precursor having the general formula:

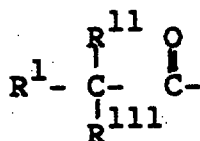


wherein R_1 is a hydrocarbyl moiety which may also incorporate heteroatoms provided that such heteroatoms are pendant therefrom, the group:

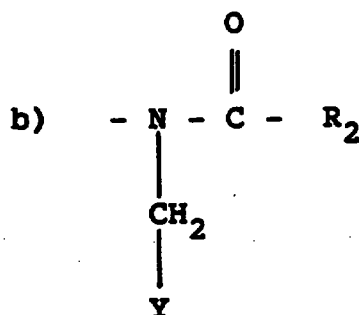
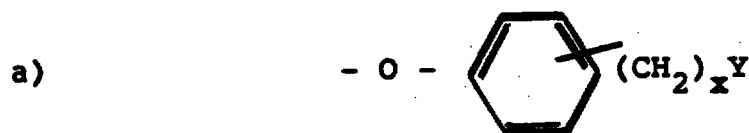


being an organic moiety of non-linear structural configuration selected from aliphatic, cycloaliphatic and arylaliphatic groups, at least one of R^{11} and R^{111} being hydrogen, the other of R^{11} and R^{111} being independently selected from hydrogen and $\text{C}_1\text{-C}_4$ alkyl groups, the group:

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being the acyl moiety of a non-linear substituted or unsubstituted alkanolic acid having a $\log P_{\text{OCT}}$ of from 1.9 to 4.1, wherein P_{OCT} is the partition coefficient of the alkanolic acid between n-octanol and water at 21°C, and L is a leaving group selected from:



wherein R_2 is an alkyl group containing from 1 to 4 carbon atoms, x is 0 or an integer from 1 to 4 and Y is selected from:

- SO_3M
- OSO_3M
- CO_2M
- $\text{N}^+(\text{R}_2)_3\text{Q}^-$
- $\text{N}(\text{R}_2)_2\text{O}$



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wherein M is H, alkali metal, alkaline earth metal ammonium or substituted ammonium and Q is a halide or methosulphate, the conjugate acid of said leaving group L having a pKa in the range from 6 to 13.

2. An aqueous laundry bleaching liquor according to claim 1 wherein the group R_1 in the peroxyalkanoic acid precursor is a hydrocarbyl moiety.
3. An aqueous laundry bleaching liquor according to either one of claims 1 and 2 wherein R^1 comprises the group:



wherein R^{1V} and R^V are each independently selected from hydrogen and C_1-C_4 alkyl groups, and the group:



comprises a C_6-C_{16} alkyl group in which at least one of R^{111} , R^{111} , R^{1V} and R^V are C_1-C_4 alkyl, R being an alkyl group such that there is a linear alkyl chain of five or more carbon atoms extending from and including the carbonyl carbon.

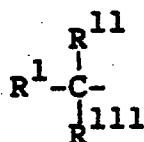
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4. An aqueous laundry liquor according to any one of claims 1-3 wherein the group:



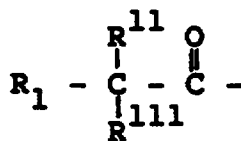
is a C_6-C_{12} group wherein R^{11} and R^{111} are hydrogen atoms.

5. An aqueous laundry liquor according to claim 4 wherein:



is a C_7-C_9 group.

6. An aqueous laundry liquor according to any one of claims 1-5 wherein the conjugate acid of leaving group L has a pKa in the range from 7 to 11.
7. An aqueous laundry liquor according to claim 6 wherein L has the formula a) in which x is O and Y is $-SO_3M$ or $-CO_2M$.
8. An aqueous laundry liquor according to claim 7 in which the group





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is either 2-ethyl hexanoyl or 3,5,5 trimethyl hexanoyl.

9. A solid laundry bleaching composition adapted to form an aqueous laundry bleaching liquor having a bland odour comprising a non-linear substituted or unsubstituted peroxyalkanoic acid precursor having a general formula as recited in any one of claims 1-8 together with a source of alkaline hydrogen peroxide comprising an alkali metal inorganic peroxyhydrate salt or a hydrogen peroxide clathrate.
10. A solid bleaching composition according to claim 9 further comprising an organic detergent surfactant.
11. A solid detergent composition according to claim 10 wherein the organic surfactant is selected from anionic, nonionic and cationic surfactants and mixtures thereof and the source of hydrogen peroxide comprises an alkali metal perborate or percarbonate or a hydrogen peroxide clathrate, the molar ratio of said alkaline hydrogen peroxide to the precursor being at least 1.5:1.
12. A solid detergent composition according to either one of claims 10 and 11 which further includes a peroxyacetic acid precursor in an amount such as to provide a non linear peroxyalkanoic acid:peracetic acid weight ratio in the range of from 3:1 to 1:5.

13. A solid detergent composition according to claim 12 wherein the peracetic acid precursor is selected from tetraacetyl ethylene diamine, tetraacetyl methylene diamine, tetraacetyl glycouril, sodium p-acetoxybenzene sulphonate, pentaacetyl glucose, octaacetyl lactose and mixtures thereof.
14. A laundry additive product adapted for addition to an aqueous laundry liquor containing a source of alkaline hydrogen peroxide, said product comprising a composition incorporating a non linear peroxyalkanoic acid precursor having a general formula as recited in any one of claims 1-8 enclosed within a container which allows access of water to the interior thereof on immersion in the liquor.
15. A laundry additive product according to claim 14 wherein the container is water impermeable and is provided with a water frangible closure.
16. A laundry additive product according to either one of claims 14 and 15 wherein the container comprises a flexible pouch or bag made of synthetic polymeric film material.
17. A laundry additive product according to either one of claims 15 and 16 wherein the water frangible closure comprises a water soluble adhesive.



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18. A laundry additive product adapted for addition to an aqueous laundry liquor containing a source of alkaline hydrogen peroxide, said product comprising a composition incorporating a non-linear peroxyalkanoic acid precursor having a general formula as hereinbefore defined in water releasable combination with a non particulate flexible substrate, the weight ratio of said precursor to said substrate being in the range of from 1:10 to 30:1.
19. A laundry additive product according to claim 18 wherein the substrate is a laminated sheet.
20. A laundry additive product according to either one of claims 18 and 19 wherein said substrate is formed of non woven fibrous material and the weight ratio of said precursor to said substrate is in the range 1:2 to 10:1.
21. A laundry additive product according to any one of claims 14-20 which further includes a peroxyacetic acid precursor in an amount such as to provide a non linear peroxyalkanoic acid:peracetic acid weight ratio in the range of from 3:1 to 1:5.
22. A laundry additive product according to any one of claims 14-21 wherein the composition incorporates one or more of an organic surfactant, a detergent builder salt or a chelating agent.



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23. A method of forming a laundry bleaching liquor having a bland odour comprising the step of adding a product in accordance with any one of claims 14-22 to an aqueous liquor containing a source of alkaline hydrogen peroxide in an amount to give a level of available oxygen of from 50 to 350 parts per million.
 24. An aqueous laundry bleaching liquor having a bland odour according to claim 1 substantially as described.
 25. A laundry detergent bleaching composition adapted to form an aqueous laundry bleaching liquor according to claim 10 substantially as described with reference to Examples 1-12 and 19-23.
 26. A laundry additive product according to claim 18 adapted for addition to aqueous laundry liquor containing a source of alkaline hydrogen peroxide substantially as described with reference to Examples 13-18.
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