**Title:** PEROXY BLEACHING COMPOSITION STABILIZED WITH ETHYLENEDIAMINE-N,N'-DISUCCINIC ACID

**Abstract**

Bleaching compositions comprising a peroxo compound and ethylenediamine-N,N'-disuccinic acid or salts thereof are provided. The bleaching compositions show good bleach stability in aqueous solution and are particularly useful in bleach processes conducted, at least in part, at temperatures > 60°C. The compositions also possess good storage stability. The bleaching compositions may be used in the bleaching of cellulose fibrous material and synthetic textiles and are also useful components of detergent compositions.
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PEROXY BLEACHING COMPOSITION STABILIZED WITH ETHYLENEDIAMINE-N, N-DISUCCINIC ACID

This invention relates to a bleaching composition comprising an active oxygen-releasing (peroxy) compound and a zero-phosphorus containing stabilizing agent, wherein the stabilizing agents permits a controlled bleaching action when the composition is used as an aqueous solution in a bleaching process. The stabilizing agent also provides for good storage stability of the product. The bleaching composition is also useful as a component of a detergent composition.

The use of peroxy compounds for bleaching purposes is well known in the art. By peroxy compound it is meant hydrogen peroxide or any of its addition compounds including inorganic perhydrate salts, such as perborates and percarbonates, or organic peroxyacids. Perborate salts are well known as components of detergent compositions for use in, for example, laundry and automatic dishwashing. Hydrogen peroxide is commonly used as a bleaching agent in, for example, textile and paper pulp bleaching processes.

In a process involving bleaching it is desirable that the bleach is released in a controlled manner throughout the process. The use of a stabilizing agent to minimize the rapid decomposition of the peroxy compound is well established in the peroxy bleaching art, because, among other things, the oxygen released by such rapid decomposition of the peroxy compound in general has no bleaching action as contrasted with the normal autodecomposition of the peroxy compound which does result in a bleaching action. In fact, the rapid
decomposition of the peroxy compound may be harmful. For example, cellulosic materials in strongly alkaline peroxy solutions are attacked by the oxygen from the rapid decomposition with the result of loss of strength by the materials. For today's laundering and dishwashing conditions the stabilizing agent should preferably be effective in alkaline solutions and under the relatively high temperature conditions which may be encountered in practice. The stabilizing agent should also be compatible with other components, which may be present in the detergent or peroxy bleaching solutions.

It is well known that the presence of certain heavy metal ions may catalyse per oxy bleach decomposition. Such heavy metal ions are inevitably present in the wash liquors of laundry and dishwashing processes, being components of many food and/or body soils. Heavy metal ions are also commonly present components of the liquors of wood pulp bleaching processes, the wood pulp tending to pick up these ions from the machinery used to masticate the wood chips and pulp.

Heavy metal sequestering or chelating agents have been employed to control the levels of free heavy metal ions in the aqueous peroxy solutions used in bleaching processes, thus acting as bleach stabilizers by preventing the heavy metal ion catalysed decomposition of the peroxy bleaches.

One chelant which at one time found widespread use as a bleach stabilizer in, for example, detergent products was ethylene diamine tetra acetate (EDTA). Concern about the environmental persistence of this chelant, which is non-biodegradable, has however mitigated a decline in its current use.

Organic phosphonate and amino alkylene poly (alkylene phosphonates) chelants are also known as bleach stabilisers being described in, for example, U.S. Patents 3, 860, 391 and 4, 239, 643. The use of phosphonate chelants in paper pulp and textile bleaching processes as well as in detergent compositions is also known. The phosphonate chelants commonly used today in such processes are however, also non-biodegradable.

Phosphorus-containing compounds have also been linked to undesirable eutrophication effects in lakes and rivers, and this has, for example, led to a dramatic reduction in the use of phosphorus-containing builder ingredients in detergent compositions.
Laundry detergent compositions containing the nil-phosphorus chelant, ethylenediamine-N,N'-disuccinic acid (EDDS) have been disclosed in EP-A-O267 653. This disclosure teaches that EDDS, when incorporated into such detergent compositions, assists in the removal of food, beverage and certain other organic stains from fabrics during the laundry process. It also teaches that EDDS may be used as a replacement for all or part of the phosphonate chelants currently used in many existing detergent products. The Applicants have discovered that when used as a component of a detergent composition EDDS assists in the removal of greasy stains. The EDDS molecule has two chiral centres. It was disclosed in EP-A-0 267 653 that the biodegradation of EDDS appeared to be optical isomer-specific with the [S,S] isomer degrading most rapidly and extensively.

The Applicants have now confirmed the optical isomer-specific nature of the biodegradation of EDDS. The [S,S] isomer is the only fully biodegradable optical isomer, being broken down essentially completely in the residence time of a normal sewage treatment process.

The Applicants have also unexpectedly discovered that the use of low levels of EDDS at specific EDDS : peroxo compound weight ratios provides excellent in use stabilization of peroxo compounds in aqueous solutions containing certain heavy metal ions. This stabilization is of particular importance at elevated solution temperatures (>60°C). Surprisingly, EDDS provides significantly better bleach stabilization than its chemical isomer EDTA under the same conditions. The Applicants have also found that incorporation of EDDS into a bleaching composition provides for improved storage stability of that composition.

EP-A-0 267 653 teaches that the EDDS-containing laundry detergent compositions described therein may also contain as optional ingredients bleaching agents, bleach activators, bleach stabilizers and the like. Peroxy compounds are not disclosed specifically in this document. EP-A-0 267 653 also makes reference to an article by J. Majer, V. Springer and B. Kopecka, published in Chem. Zvesti. 20(6) : 414-422 (1966) (CAS abstract 65 : 11738f). This article gives stability constants for the complexes of EDDS with the heavy metal ions Fe³⁺, Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Pb²⁺ and Cd²⁺ and compares these to the corresponding stability constants for the complexes with
EDTA. For each of these metal ions, excepting Cu^{2+}, the stability constant for the EDDS complex is lower than for the EDTA complex. For Cu^{2+} the stability constants are practically the same. The Applicant's finding that at elevated temperatures EDDS is a better bleach stabilizer than EDTA are therefore even more surprising in the light of the disclosure of this article.

It is therefore an object of this invention to provide bleaching compositions comprising a peroxo compound and the nil-phosphorus chelant, EDDS wherein this composition shows good bleach stability in aqueous solution, particularly at solution temperatures >60°C.

According to one aspect of the present invention there is provided a bleaching composition comprising:

(a) a peroxo compound, selected from hydrogen peroxide and the addition compounds of hydrogen peroxide, organic peroxycarboxylic acids, and mixtures thereof; and

(b) from 0.05% to 2% by weight of the composition of ethylenediamine-N,N'-disuccinic acid, or alkali metal, alkaline earth, ammonium or substituted ammonium salts thereof, or mixtures thereof, wherein the weight ratio of said peroxo compound to said ethylenediamine-N,N'-disuccinic acid lies in the range from 800 : 1 to 10 : 1.

The weight ratio of said peroxo compound to said ethylene diamine-N,N'-disuccinic acid preferably lies in the range from 400 : 1 to 20 : 1, more preferably from 200 : 1 to 40 : 1, and most preferably from 150 : 1 to 50 : 1.

The peroxo compound is preferably present at a level of from 0.5% to 60%, more preferably from 1% to 40%, most preferably from 2% to 25% by weight of the bleaching composition.

The bleaching compositions of the invention may be used in essentially any bleaching process. According to one aspect of the present invention the bleaching process will employ an aqueous alkaline solution of the bleaching composition, with a preferred pH range for said solution lying in the range from 7.5-12.5, more preferably from 9-12, most preferably from 9.5 to 11.5.
According to a further aspect of the present invention the bleaching process will employ a solution of an acidic per oxy compound containing bleach formulation. Such formulations are commonly employed in bleach additive or household/hard surface cleaner applications. Such acidic bleach formulations typically have a pH of from 0.5 to 6, preferably from 1 to 5.

Preferably a bleaching process in accord with the invention will be carried out, at least in part, at a temperature greater than 60°C.

The first essential component of the bleaching compositions of the invention is a per oxy compound. The per oxy compound may be hydrogen peroxide or any of the addition compounds of hydrogen peroxide, or organic peroxy acid, or mixtures thereof. By addition compounds of hydrogen peroxide it is meant compounds which are formed by the addition of hydrogen peroxide to a second chemical compound, which may be for example an inorganic salt, urea or organic carboxylate, to provide the addition compound. Examples of the addition compounds of hydrogen peroxide include inorganic perhydrate salts, the compounds hydrogen peroxide forms with organic carboxylates, urea, and compounds in which hydrogen peroxide is clathrated.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. Salts in which hydrogen peroxide is clathrated are described in GB-A-1494953.

Sodium percarbonate is a preferred inorganic perhydrate for inclusion in granular bleaching compositions in accordance with the invention. This may be incorporated as either the monohydrate of empirical formula NaBO2 . H2O2 . 3H2O.

The bleaching compositions of the invention may and any compositions into which they may be incorporated may be of essentially any physical form such as solid, including powders, bars and granules, or fluid, including liquids, gels and pastes. When the per oxy compound is hydrogen peroxide however, the bleaching composition will generally comprise a concentrated solution of the hydrogen peroxide together with the EDDS. When the per oxy compound is an
inorganic perhydrate salt the bleaching composition will generally be solid, preferably granular in nature. The inorganic perhydrate salt may be included in such a granular composition as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium percarbonate, which is a highly preferred perhydrate for inclusion in granular bleaching compositions in accordance with the invention, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3.3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in coated form. The most preferred coating material comprises a mixed salt of an alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_2\text{SO}_4.\text{nNa}_2\text{CO}_3$ wherein n is form 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material is sodium silicate of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio from 1.6 : 1 to 3.4 : 1, preferably 2.8 : 1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Magnesium silicate can also be included in the coating. Other suitable coating materials include the alkali and alkaline earth metal sulphates and carbonates.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of particular usefulness in the compositions. The corresponding organic peroxyacid, namely peroxymonopersulfuric acid is also useful.

Where the bleaching processes utilizing the bleaching compositions of the invention are carried out at least in part at temperatures lower than about 60°C the bleaching compositions of the invention will also preferably contain
additional bleaching agents more suited to low temperature bleaching. These will include, for example peroxyacid bleach precursor (bleach activator).

Whilst, the principal advantage of the presence of EDDS in the bleaching compositions of the invention lies in its stabilization of peroxy compounds when used in high temperature (>60°C) bleaching processes it still acts as an effective chelant at lower solution temperatures. Thus, the heavy metal ion chelation provided by EDDS may also stabilize any organic peroxyacid bleach components which are present as active bleaching agents at these lower solution temperatures.

EDDS also provides improved storage stability characteristics when incorporated into bleach containing compositions. Such improved storage stability characteristics are particularly observed when the bleach-containing compositions are formulated as alkaline detergent compositions, or as acidic formulations possessing a pH of from 0.5 to 6. The achievement of good storage stability characteristics for acidic bleaching formulations is known to be a particular problem in the art.

The peroxyacid bleach precursors probably contain one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836988, 864,798, 1147871 and 2143231 and imides such as are disclosed in GB-A-855735 & 1246338.

Particularly preferred precursor compounds are the N,N,N¹,N¹ tetra acetylated compounds of formula

\[
\begin{align*}
&\text{O} \\
&\text{CH}_3 - \text{C} \\
&\text{N} - \text{(CH}_2\text{)}_x - \text{N} \\
&\text{CH}_3 - \text{C} \\
&\text{O}
\end{align*}
\]

\[
\begin{align*}
&\text{O} \\
&\text{C} - \text{CH}_3 \\
&\text{N} - \text{(CH}_2\text{)}_x - \text{N} \\
&\text{C} - \text{CH}_3 \\
&\text{O}
\end{align*}
\]
wherein \( x \) can be \( O \) or an integer between 1 & 6.

Examples include tetra acetyl methylene diamine (TAMD) in which \( x = 1 \), tetra acetyl ethylene diamine (TAED) in which \( x = 2 \) and tetraacetyl hexylene diamine (TAHD) in which \( x = 6 \). These and analogous compounds are described in GB-A-907356. The most preferred peroxycacid bleach precursor is TAED.

Another preferred class of peroxycacid bleach activator compounds are the amide substituted compounds of the following general formulae:

\[
R^1 - C - N - R^2 - C - L \quad \text{or} \quad R^1 - N - C - R^2 - C - L
\]

\[
\text{wherein } R^1 \text{ is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, } R^2 \text{ is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and } R^5 \text{ is } H \text{ or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and } L \text{ can be essentially any leaving group. } R^1 \text{ preferably contains from about 6 to 12 carbon atoms. } R^2 \text{ preferably contains from about 4 to 8 carbon atoms. } R^1 \text{ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for } R^2. \text{ The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. } R^5 \text{ is preferably } H \text{ or methyl. } R^1 \text{ and } R^5 \text{ should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.}

Other peroxycacid bleach precursor compounds include sodium nonanoyloxy benzene sulphonate, sodium trimethyl hexanoyloxy benzene sulphonate, sodium acetoxy benzene sulphonate and sodium benzoyloxy benzene sulphonate as disclosed in, for example, EP-A-0341947.
The compositions of the invention may contain as the peroxy compound organic peroxyacids of which a particularly preferred class are the amide substituted peroxyacids of general formulae:

$$\begin{align*}
R^1 - C - N - R^2 - C - OOH \\
\text{or} \\
R^1 - N - C - R^2 - C - OOH \\
O \quad O \\
O \quad R^5 \\
O \quad R^5
\end{align*}$$

where $R^1$, $R^2$ and $R^5$ are as defined previously for the corresponding amide substituted peroxyacid bleach activator compounds.

Other organic peroxyacids include the dicacly peroxides and dialkyl peroxides. Suitable are diperoxy dodecanedioic acid, diperoxy tetra decanedioic acid, diperoxyhexadecanedioic acid, mono- and diperoxyhexadecanedioic acid, mono- and diperoxyhexadecanedioic acid, monoperoxy phthalic acid, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

When incorporated as components of liquid, particularly acidic liquid, bleaching compositions the peroxy compound, and in particular any organic peroxyacids, may be dissolved or dispersed or be incorporated as emulsions or suspensions.

The bleaching compositions of the invention contain, as the second essential component from 0.05% to 2% by weight of the composition, preferably from 0.05% to 1% by weight, most preferably from 0.1% to 0.5% by weight of ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Examples of such preferred sodium salts of EDDS include Na$_3$ EDDS. Examples of such preferred magnesium complexes of EDDS include Mg EDDS and Mg$_2$ EDDS.

The magnesium complexes are the most preferred for inclusion in granular compositions in accord with the invention. These complexes may be added to the compositions as such, or they may be formed during the process for making the composition by the reaction of an inert magnesium salt such as MgCl$_2$ or MgSO$_4$ with an EDDS compound present as either the free acid, or
as another salt or complex. Where the EDDS compound is added in the making process together with the inert magnesium salt it is preferred that the molar ratio of magnesium to EDDS should be greater than 1:1, preferably greater than 3:1, to ensure formation of the desired magnesium complexes.

The structure of the acid form of EDDS is as follows.

\[
\begin{array}{c}
H-N-\text{CH}_2-\text{CH}_2-N-H \\
\text{CH}_2-\text{CH} \\
\text{COOH} \quad \text{COOH}
\end{array}
\quad \begin{array}{c}
\text{CH} \\
\text{CH}_2-\text{CH} \\
\text{COOH} \quad \text{COOH}
\end{array}
\]

EDDS can be synthesised, for example, from readily available, inexpensive starting material such as maleic anhydride and ethylene diamine as follows.

\[
2 \quad \begin{array}{c}
\text{O} \\
\text{C=O} \\
\text{CH} \\
\text{O=C} \\
\text{CH}
\end{array} + \begin{array}{c}
\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \\
\text{NaOH} \quad \Delta \quad \text{EDDS}
\end{array}
\]

A more complete disclosure of methods for synthesising EDDS from commercially available starting materials can be found in US Patent 3,158,635, Kezerian and Ramsay, issued November 24, 1964.

The synthesis of EDDS from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R], [S,S], and [S,R], due to the two asymmetric carbon atoms. The biodegradation of EDDS is optical isomer-specific, with the [S,S] isomer degrading most rapidly and extensively, and for this reason the [S,S] isomer is most preferred for inclusion in the compositions of the invention.

The [S,S] isomer of EDDS can be synthesised from L-aspartic acid and 1,2-dibromoethane, as follows.

\[
2 \quad \begin{array}{c}
\text{CH}_2-\text{CH} \\
\text{COOH} \quad \text{COOH}
\end{array} + \begin{array}{c}
\text{Br-CH}_2-\text{CH}_2-\text{Br} \\
\text{NaOH} \quad \Delta \quad [S,S] \text{EDDS}
\end{array}
\]
A more complete disclosure of the reaction of L-aspartic acid with 1,2-dibromoethane to form the [S,S] isomer of EDDS can be found in Neal and Rose, Stereospecific Ligands and Their Complexes of Ethylenediamine-disuccinic Acid, *Inorganic Chemistry*, Vol. 7 (1968), pp. 2405-2412.

The bleaching compositions of the invention are useful in the bleaching of cellulosic fibrous material. The term cellulosic fibrous material as used herein has reference to wood, cotton, linen, jute and other materials of a cellulosic nature, and also includes individual fibres, for example wood pulp or cotton fibre, as well as yarns, tows, webs, fabrics (woven or non-woven) and other aggregates of such fibres. The bleaching compositions of the invention are also useful in the bleaching of synthetic textiles including polyamides, viscose, rayon, and polyesters.

The bleaching compositions of the invention are also useful in cleaning compositions. These cleaning compositions may be used in essentially any washing, laundering or cleaning processes in which bleaching is required. Thus, the cleaning compositions may be used in home or industrial laundering or automatic dishwashing processes, as laundry additive compositions, stain pretreat compositions, carpet and upholstery cleaners, and in any process involving the cleaning of hard surfaces such as bottle washing, dairy cleaning and kitchen and bathroom cleaning processes, including for example toilet bowl cleaning.

In processes for the bleaching of cellulosic fibre or synthetic textiles the bleaching compositions of the invention are used in an aqueous solution. The most preferred peroxy compound for use in such processes is hydrogen peroxide. The pH of the aqueous peroxy solution is often adjusted with inorganic alkali metal basic materials, such as sodium hydroxide, sodium carbonate, sodium silicate and mixtures thereof. The optimum pH lies somewhere between 7.5 to 12.5. Usually, if the pH is higher than about 12.5 the peroxy-compounds rapidly decompose so that it is difficult to control a proper bleaching rate without undue damage to the fibres. At pH values lower than about 7.5 the rate of bleaching in most cases is slow to the extent of being uneconomical for bleaching.
Whilst silicates, especially sodium silicate may be used to provide alkalinity in the peroxo solutions for use in the bleaching of cellulosic fibres its tendency to form as deposits on the fibres being bleached means that its use is preferably kept to a minimum. Most preferably, the peroxo solutions for use in the bleaching of cellulosic fibres and synthetic textiles using the bleaching compositions of the invention contain no sodium silicate.

The concentration of the EDDS stabilizing agent in the cellulose fibre or synthetic textile bleaching peroxo solutions can vary depending upon, inter alia, concentration of the peroxo solution, type of peroxo compound used, pH, temperature and the like, and usually for normal concentrations of peroxo solutions and with conventional cellulose fibre/synthetic textile bleaching methods, the EDDS is preferably present in concentrations from 0.0005% to 0.5% by weight with concentrations of from 0.001% to 0.1% by weight being especially preferred.

The methods for bleaching using the peroxo solutions containing the bleaching compositions of the present invention vary widely, as for example, from using the peroxo solutions at temperatures of from about 70°C to about 100°C for periods of time from about 30 minutes to about 6-8 hours, as well as continuous bleaching methods which entail the use of the peroxo solutions at normal temperatures, i.e., about 25°C and contacting the cellulose material by saturation, removing the excess moisture and exposing the cellulose material to saturated steam at temperatures form about 100°C to about 135°C, for period of time from a few seconds (about 20) to about 1 hour and even longer in some cases. U.S. Patents 2,839,353, 2,960,383, and 2,983,568 are illustrative of being representative of continuous peroxo bleaching methods.

The bleaching compositions of the invention may also be incorporated into compositions for use in essentially any laundering, washing or cleaning processes. Laundry compositions incorporating the bleaching compositions of the invention can be formulated as granular compositions and heavy duty liquid compositions.

The compositions may in addition comprise in general terms those ingredients commonly found in detergent products which may include organic surfactants, detergent builders, anti-redeposition and soil suspenson agents, suds
suppressors, enzymes, optical brighteners, photoactivated bleaches, perfumes, filler salts, anti-corrosion agents and colours.

Laundry detergent compositions may also comprise fabric softening and antistatic agents.

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Mixtures of anionic surfactants are suitable herein, particularly blends of sulphate, sulphonate and/or carboxylate surfactants. Mixtures of sulphonate and sulphate surfactants are normally employed in a sulphonate to sulphate weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C_{12}-C_{18} fatty source, preferably from a C_{16}-C_{18} fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants in such sulphonate sulphate mixtures are alkyl sulphates having from 12 to 22, preferably 16 to 18 carbon atoms in the alkyl radical.

Another useful surfactant system comprises a mixture of two alkyl sulphate materials whose respective mean chain lengths differ from each other. One such system comprises a mixture of C_{14}-C_{15} alkyl sulphate and C_{16}-C_{18} alkyl sulphate in a weight ratio of C_{14}-C_{15}: C_{16}-C_{18} of from 3:1 to 1:1. The alkyl sulphates may also be combined with alkyl ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. The cation in each instance is again an alkali metal, preferably sodium.

Another highly preferred anionic surfactant system comprises a mixture of a C_{12}-C_{20} alkyl sulfate salt with a water soluble C_{11}.C_{18} alkyl ethoxysulfate
salt containing an average of from 1 to 7 ethoxy groups per mole wherein the weight ratio of alkyl sulfate to alkyl ethoxysulfate salt lies in the range from 2 : 1 to 19 : 1, more preferably from 3 : 1 to 12 : 1 and most preferably from 3.5 : 1 to 10 : 1.

The alkyl sulfate salts may be derived from natural or synthetic hydrocarbon sources. Preferred examples of such salts include the substantially branched C₁₄-C₁₅ alkyl sulfate salts, that is where the degree of branching of the C₁₄-C₁₅ alkyl chain is greater than about 20%. Such substantially branched C₁₄-C₁₅ alkyl sulfate salts are usually derived from synthetic sources. Also preferred are C₁₆-C₂₀ alkyl sulfate salts which are usually derived from natural sources such as tallow fat and marine oils.

The C₁₁-C₁₈ alkyl ethoxysulfate salt comprises a primary alkyl ethoxysulfate which is derived from the condensation product of a C₁₁-C₁₈ alcohol condensed with an average of from one to seven ethylene oxide groups, per mole. Preferred are the C₁₂-C₁₅ alkyl ethoxysulfate salts with an average of from one to five ethoxy groups per mole, and most preferably with an average of from one to three ethoxy groups per mole.

Thus C₁₁-C₁₈ alcohol itself can be obtained from natural or synthetic sources. Thus, C₁₁-C₁₈ alcohols, derived from natural fats, or Ziegler olefin build-up, or OXO synthesis can form suitable sources for the alkyl group. Examples of synthetically derived materials include Dobaño 25 (RTM) sold by Shell Chemicals (UK) Ltd which is a blend of C₁₂-C₁₅ alcohols, Ethyl 24 sold by the Ethyl Corporation, a blend of C₁₃-C₁₅ alcohols in the ratio 67% C₁₃, 33% C₁₅ sold under the trade name Lutensol by BASF GmbH and Synperonic (RTM) by ICI Ltd., and Lial 125 sold by Liquichimica Italiana. Examples of naturally occurring materials from which the alcohols can be derived are coconut oil and palm kernel oil and the corresponding fatty acids. The level of C₁₁-C₁₈ alkyl ethoxysulfate is preferably from 0.5% to 10% more preferably from 0.5% to 5% and most preferably from 1% to 3% by weight of the composition.
Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula

$$\text{R-CON (R}^1\text{) CH}_2\text{ COOM}$$

wherin $\text{R}$ is a C$_5$-C$_{17}$ linear or branched alkyl or alkenyl group, $\text{R}^1$ is a C$_1$-C$_4$ alkyl group and $\text{M}$ is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C$_{12}$-C$_{14}$), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

One class of nonionic surfactants useful in the present invention comprises condensates of ethylene oxide with a hydrophobic moiety, providing surfactants 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 (lipophilic) 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.

Especially preferred nonionic surfactants of this type are the C$_9$-C$_{15}$ primary alcohol ethoxylates containing an average of from 3-8 moles of ethylene oxide per mole of alcohol, particularly the C$_{14}$-C$_{15}$ primary alcohols containing an average of from 6-8 moles of ethylene oxide per mole of alcohol and the C$_{12}$-C$_{15}$ primary alcohols containing an average of from 3-5 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula

$$\text{RO (C}_n\text{H}_{2n}\text{O}_n\text{)}_t\text{Z}_x$$

wherein $\text{Z}$ is a moiety derived from glucose; $\text{R}$ is a saturated hydrophobic alkyl group that contains from 6 to 18 carbon atoms; $t$ is from 0 to 10 and $n$ is 2 or 3; $x$ is from 1.1 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds
of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

Another preferred nonionic surfactant is a polyhydroxy fatty acid amide surfactant compound having the structural formula:

\[
\begin{array}{c}
\text{O} \\
\text{R}^1 \\
\text{R}^2 - \text{C} - \text{N} - \text{Z}
\end{array}
\]

wherein: \( R^1 \) is H, C\(_1\)-C\(_4\) hydrocarbaryl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C\(_1\)-C\(_4\) alkyl, more preferably C\(_1\) or C\(_2\) alkyl, most preferably C\(_1\) alkyl (i.e., methyl); and \( R^2 \) is a C\(_5\)-C\(_{31}\) hydrocarbaryl, preferably straight chain C\(_7\)-C\(_{19}\) alkyl or alkenyl, more preferably straight chain C\(_9\)-C\(_{17}\) alkyl or alkenyl, most preferably straight chain C\(_{11}\)-C\(_{17}\) alkyl or alkenyl, or mixture thereof; and \( Z \) is a polyhydroxyhydrocarbaryl having a linear hydrocarbaryl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. \( Z \) preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably \( Z \) is a glycetyl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for \( Z \). It should be understood that it is by no means intended to exclude other suitable raw materials. \( Z \) preferably will be selected from the group consisting of

\[\text{CH}_2-(\text{CHOH})_n\text{CH}_2\text{OH}, \quad \text{CH}(\text{CH}_2\text{OH})(\text{CHOH})_{n-1}\text{CH}_2\text{OH}, \quad \text{CH}_2-(\text{CHOH})_2(\text{CHOH})\text{CH}_2\text{OH}, \quad \text{CH}_2-(\text{CHOH})_3\text{CH}_2\text{OH}, \quad \text{CH}_2-(\text{CHOH})_4\text{CH}_2\text{OH},\]

where \( n \) is an integer from 3 to 5, inclusive, and \( R' \) is H or a cyclic or aliphatic monosaccharide, and alkoxylated derivatives thereof. Most preferred are glycetyl wherein \( n \) is 4, particularly \( \text{CH}_2-(\text{CHOH})_4\text{CH}_2\text{OH}. \)
In Formula (I), R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

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

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymalto-trirotityl, etc. Preferred compound are N-methyl N-1deoxyglucityl C₁₄-C₁₈ fatty acid amides.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C₆-C₂₀, preferably C₁₀-C₁₄ N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C₈-C₁₆, preferably C₁₀-C₁₄ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Laundry detergent compositions incorporating the bleaching compositions of the invention comprise from 3% to 30% of surfactant but more usually comprise from 5% to 20%, more preferably from 7% to 15% surfactant by weight of the compositions.

Machine dishwashing detergent compositions incorporating the bleaching compositions of the invention comprise from 0% to 10% by weight, preferably from 0.5% to 10% by weight, most preferably from 1% to 5% of surfactant by weight of the compositions. The surfactants may be selected from anionic, cationic, nonionic, amphotonic or zwitterionic surfactants. Most preferably the surfactants are low-foaming. A typical listing of surfactants for inclusion in automatic dishwashing detergent compositions is given in EP-A-0414 549.
Most preferred are low-foaming nonionic surfactants, especially the water soluble ethoxylated C₆-C₁₆ fatty alcohols and C₆-C₁₆ mixed ethoxylated/propoxylated fatty alcohols and mixtures thereof. Preferably, the ethoxylated fatty alcohols are the C₁₀-C₁₆ ethoxylated fatty alcohols with a degree of ethoxylation of from 5 to 50, most preferably these are the C₁₂-C₁₆ ethoxylated fatty alcohols with a degree of ethoxylation from 8 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Combinations of surfactant types are preferred, more especially anionic-nonionic and also anionic-nonionic-cationic blends. Particularly preferred combinations are described in GB-A-2040987 and EP-A-0087914. Although the surfactants can be incorporated into the compositions as mixtures, it is preferable to control the point of addition of each surfactant in order to optimise the physical characteristics of the composition and avoid processing problems.

Preferred modes and orders of surfactant addition are described hereinafter.

Another highly preferred component of the detergent compositions of the invention is a detergent builder system comprising one or more other non-phosphate detergent builders. These can include, but are not restricted to, crystalline layered sodium silicates, carbonates borates, alkali metal aluminosilicates, monomeric polycarboxylates, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, silicates and mixtures of any of the foregoing.

Preferred non-phosphate builder salts are the crystalline layered sodium silicates of the general formula

\[ \text{NaMSi}_x\text{O}_{2x+y}+1\text{.H}_2\text{O} \]
wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α-, β-, γ- and δ- forms of Na₂Si₂O₅. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is δ-Na₂Si₂O₅, NaSKS-6.

These materials are processed into free flowing solids with a particle size of from 150 to 1000 micrometers and a bulk density of at least 800 g/litre preferably approximately 900 g/litre. However, as made, the crystals are fragile and break down easily into particles of size less than 100 micrometers.

The laundry detergent compositions incorporating the bleaching compositions of the present invention preferably comprise crystalline layered sodium silicate at a level of from 1% to 80% by weight of the composition, more preferably from 5% to 40% and most preferably from 7% to 20% by weight.

The crystalline layered sodium silicate material is preferably present as a particulate in intimate admixture with a solid, water-soluble ionisable material. The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof. The primary requirement is that the material should contain at least one functional acidic group of which the pKa should be less than 9, providing a capability for at least partial neutralisation of the hydroxyl ions released by the crystalline layered silicate. Surprisingly, it has been found for the purposes of the present invention, that the ionisable material need not have a pH < 7 in solution, or be present in an amount capable of providing hydrogen ions in stoichiometric parity with the hydroxyl ions produced by dissolution of the crystalline silicate. In fact neutralisation of the ionisable material during storage of the particulate, whilst causing a loss in fabric damage benefit, does not eliminate it.
The ionisable material should also have a mean particle size not greater than 300 micrometers and preferably not greater than 100 micrometers. This facilitates uniform distribution of the ionisable material and the crystalline silicate and is believed to enhance localised pH reduction when the particulate dissolves in the wash liquor.

Suitable organic acids include ascorbic, citric, glutaric, gluconic, glycolic, malic, maleic, malonic, oxalic, succinic and tartaric acids, 1 hydroxy ethane 1,1-diphosphonic acid (EHDP), amino poly methylene phosphonic acids such as NTMP, EDTMP & DETPMP, and mixtures of any of the foregoing. Suitable acid salts include sodium hydrogen carbonate, sodium hydrogen oxalate, sodium hydrogen sulphate, sodium acid pyrophosphate, sodium acid orthophosphate, sodium hydrogen tartrate or mixtures of any of the foregoing.

The particulate mixture of crystalline layered silicate and solid water soluble ionisable material will have a pH of at least 10 (as measured on a 1% solution in 20°C distilled water) and more usually will have a pH of at least 11, normally at least 11.5.

The incorporation of other ingredients additional to the crystalline layered silicate and ionisable water soluble compound can be advantageous particularly in the processing of the particulate and also in enhancing the stability of detergent compositions in which the particulates are included. In particular, certain types of agglomerates may require the addition of one or more binder agents in order to assist in binding the silicate and ionisable water soluble material so as to produce particulates with acceptable physical characteristics. The binder agents may be present at a level of from 0% to 20% by weight of the composition. Preferably, the binder agents will be in intimate admixture with the silicate and ionisable water soluble material. Preferred binder agents have a melting point between 30°C-70°C. The binder agents are preferably present in amounts from 1-10% by weight of the composition and most preferably from 2-5% by weight of the composition.
Preferred binder agents include the C_{10}-C_{20} alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C_{15}-C_{20} primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol.

Other preferred binder agents include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols with an average weight of from 600 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C_{10}-C_{20} alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole. Further examples of binder agents in accord with the invention include the C_{10}-C_{20} mono- and diglycerol ethers and also the C_{10}-C_{20} fatty acids. Solutions of certain inorganic salts including sodium silicate are also of use for this purpose.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acid or their salts are other examples of binder agents in accord with the invention.

The particulate can also include other components that are conventional in detergent compositions, provided that these are not incompatible per se and do not interfere with the building function of the crystalline layered silicate. Thus the particulate can include up to 50% by weight of the particulate of an anionic, nonionic, ampholytic or zwitterionic surfactant or a mixture of any of these and certain preferred particulate embodiments incorporate surfactants. Examples of such surfactants are described more fully hereinafter. However it is important that any surfactant material that is incorporated into the particulate does not introduce a level of free (unbound) moisture that can even partially dissolve the crystalline layered silicate. For this purpose, the surfactant should be solid and should preferably contain no more than about
5% free (unbound) moisture, preferably no more than 2% free moisture and most preferably less than 1% free moisture.

Other ingredients can also be incorporated in a total amount of up to 50% by weight of the particulate, subject to the same conditions set out above for the inclusion of surfactants. Thus such optional ingredients should preferably be solid at normal (ambient) temperatures, and should contain no more than 5% by weight of free (unbound) moisture, preferably less than 1%.

Non-aqueous liquid components can be incorporated in amounts of up to 20% by weight of the particulate provided that the crystalline layered silicate does not have an appreciable solubility in such components. This also applies to normally solid components applied in a molten form to serve as agglomeration/coating agents for the particulate.

The particulates can take a variety of physical forms such as extrudates, marumes, agglomerates, flakes or compacted granules. A preferred process for preparing compacted granules comprising crystalline layered silicate and a solid, water-soluble ionisable material has been disclosed in the commonly assigned British Application No. 9108639.7 filed on 23 April 1991 (Attorney’s Docket No. CM369F).

Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate zeolites have the unit cell formula

$$\text{Na}_z \left[ (\text{AlO}_2)_z (\text{SiO}_2)_y \right] \cdot x\text{H}_2\text{O}$$

wherein $z$ and $y$ are at least 6; the molar ratio of $z$ to $y$ is from 1.0 to 0.5 and $x$ is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The above aluminosilicate ion exchange materials are further characterised by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined
by conventional analytical techniques such as, for example, microscopic
determination utilizing a scanning electron microscope or by means of a laser
granulometer. The aluminosilicate ion exchange materials are further
characterised by their calcium ion exchange capacity, which is at least 200 mg
equivalent of CaCO₃ water hardness/g of aluminosilicate, calculated on an
anhydrous basis, and which generally is in the range of from 300 mg eq./g to
352 mg eq./g. The aluminosilicate ion exchange materials herein are still
further characterised by their calcium ion exchange rate which is at least 130
mg equivalent of CaCO₃/litre/minute/(g/litre) [2 grains Ca⁺⁺/
gallon/minute/gram/gallon]) of aluminosilicate (anhydrous basis), and which
generally lies within the range of from 130 mg equivalent of
CaCO₃/litre/minute/(gram/litre) [2 grains/gallon/minute/ (gram/gallon)] to
390 mg equivalent of CaCO₃/litre/minute/ (gram/litre) [6
grains/gallon/minute/(gram/gallon)], based on calcium ion hardness.

Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange
rate of at least 260 mg equivalent of CaCO₃/litre/ minute/ (gram/litre) [4
grains/gallon/minute/(gram/gallon)].

Aluminosilicate ion exchange materials useful in the practice of this invention
are commercially available and can be naturally occurring materials, but are
preferably synthetically derived. A method for producing aluminosilicate ion
synthetic crystalline aluminosilicate ion exchange materials useful herein are
available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X,
Zeolite HS, Zeolite MAP and mixtures thereof. In an especially preferred
embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A
and has the formula

\[ \text{Na}_{12} \left( \left( \text{AlO}_2 \right)_{12} \left( \text{SiO}_2 \right)_{12} \right) \times \text{H}_2 \text{O} \]

wherein x is from 20 to 30, especially 27. Zeolite X of formula Na₈₆
\[ \left( \text{AlO}_2 \right)_{86} \left( \text{SiO}_2 \right)_{106} ] \]. 276 H₂O is also suitable, as well as Zeolite HS of
formula Na₆ \[ \left( \text{AlO}_2 \right)₆ \left( \text{SiO}_2 \right)₆ ] 7.5 H₂ O).
Suitable water-soluble monomeric or oligomeric carboxylate builders can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity/constant (pK₁) of less than 9, preferably of between 2 and 8.5, more preferably of between 4 and 7.5.

The logarithmic acidity constant is defined by reference to the equilibrium

$$\text{H}^+ + \text{A}^- \rightleftharpoons \text{HA}$$

where A is the fully ionized carboxylate anion of the builder salt.

The equilibrium constant for dilute solutions is therefore given by the expression

$$K_1 = \frac{[\text{HA}]}{[\text{H}^+][\text{A}^-]}$$

and pK₁ = log₁₀K₁.

For the purposes of this specification, acidity constants are defined at 25°C and at zero ionic strength. Literature values are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, London): where doubt arises they are determined by potentiometric titration using a glass electrode.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates having the general formulae

(a)

(b)
wherein $R_1$ represents $H$, C$_{1-30}$ alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethyleneoxy moiety containing up to 20 ethyleneoxy groups; $R_2$ represents $H$, C$_{1-4}$ alkyl, alkenyl or hydroxy alkyl, or alkaryl, sulfo, or phosphono groups; $X$ represents a single bond; O; S; SO; SO$_2$; or NR$_1$; $Y$ represents $H$; carboxy; hydroxy; carboxymethyloxy; or C$_{1-30}$ alkyl or alkenyl optionally substituted by hydroxy or carboxy groups; $Z$ represents $H$; or carboxy; $m$ is an integer from 1 to 10; $n$ is an integer from 3 to 6; $p$, $q$ are integers from 0 to 6, $p + q$ being from 1 to 6; and wherein, $X$, $Y$, and $Z$ each have the same or different representations when repeated in a given molecular formula, and wherein at least one $Y$ or $Z$ in a molecule contain a carboxyl group.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethyleneoxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in
British Patent No. 1,379,241, lactoxyxuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of detergent compositions in accordance with the present invention.

Other suitable water soluble organic salts are the 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 the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their
copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000. These materials are normally used at levels of from 0.5% to 10% by weight more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

The detergent compositions incorporating the bleaching compositions of the present invention will comprise non-phosphate detergent builder compounds at a level of from 1% to 80% by weight of the compositions, more preferably from 10% to 60% by weight and most preferably from 20% to 50% by weight.

Within the preferred laundry detergent compositions, sodium aluminosilicate such as Zeolite A will comprise from 20% to 60% by weight of the total amount of builder, a monomeric or oligomeric carboxylate will comprise from 5% to 30% by weight of the total amount of builder and the crystalline layered silicate will comprise from 10% to 65% by weight of the total amount of builder. In such compositions the builder system preferably also incorporates a combination of auxiliary inorganic and organic builders such as sodium carbonate and maleic anhydride/acrylic acid copolymers in amounts of up to 35% by weight of the total builder.

The detergent compositions may contain optional chelant ingredients. Such optional chelants may include the organic phosphonates, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as a complex of either an alkali or alkaline metal ion, the molar ratio of said metal ion to said phosphonate compound being at least 1 : 1. Such complexes are described in US-A-4,259,200. Preferably, the organic phosphonate compounds where present are in the form of their magnesium salt. The level of phosphorus containing chelants in the compositions of the invention is preferably minimised, with their complete exclusion from the compositions being most preferred.
Silicates are useful components of automatic dishwashing detergent compositions incorporating the bleaching compositions of the present invention. Suitable silicates include the water soluble sodium silicates with an SiO$_2$ : Na$_2$O ratio of from 1.0 to 2.8. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO$_2$ : Na$_2$O ratio of 2.0 is most preferred. Silicates are present in the machine dishwashing detergent compositions at a level of from 5% to 50% by weight of the composition, more preferably from 10% to 40% by weight.

Whilst soluble silicates serve a variety of purposes in conventional laundry detergent formulations, their presence may be unnecessary in detergent compositions incorporating crystalline layered silicate material. However as the crystalline layered silicate, which forms part of the builder system of the detergent composition, must be added as a dry mix ingredient, soluble silicates may still be useful as structurants in the spray dried granules that normally form part of a laundry detergent composition. This is particularly desirable if the spray dried granule does not incorporate an aluminosilicate builder and would otherwise comprise only organic materials. Suitable silicates are those having an SiO$_2$:Na$_2$O ratio in the range from 1.6 to 3.4, ratios from 2.0 to 2.8 being preferred.

The detergent compositions incorporating the bleaching compositions of the present invention will generally include an inorganic perhydrate salt, normally in the form of the sodium salt. Suitable inorganic perhydrate salts have been described hereinbefore. The bleaching composition will usually be incorporated to give a perhydrate level of from 3% to 40% by weight, more preferably from 5% to 30% by weight and most preferably from 10% to 25% by weight of the detergent composition.

The detergent compositions incorporating the bleaching compositions of the present invention will also generally include peroxyacid bleach precursors (bleach activators). Suitable peroxyacid bleach precursors have been described hereinbefore. The peroxyacid bleach precursors are normally incorporated at a level of from 1% to 20%, more preferably from 1% to 15%, most preferably from 3% to 10% by weight of the compositions.
The detergent compositions may also contain organic per oxyacids at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

Detergent compositions in which solid peroxybleach precursors are protected via an acid coating to minimise fabric colour damage are disclosed in the Applicant's copending British Application No. 9102507.2 filed February 6 1991.

Anti-redeposition and soil-suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, homo- or co-polymeric polycarboxylic acids or their salts and ployamino compounds. Polymers of this type include the polyacrylates and copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer disclosed in detail in EP-A-137669. Polyamino compounds such as those derived from aspartic acid are disclosed in EP-A-305282, EP-A-305283 and EP-A-351629. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts 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.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4₁-bis-(2-diethanolamino-4-anilino -s- triazin-6- ylmino)stilbene-2:2₁ disulphonate, disodium 4,4₁-bis-(2-morpholino -4-anilino-2-triazin-6-ylaminostilbene-2:2₁-disulphonate, disodium 4, 4₁-bis-(2,4-dianilino-s-triazin-
6-ylamino)stilbene-2:21 - disulphonate, monosodium 41,411-bis-(2,4-dianilinostriazin-6-ylamino)stilbene-2- sulphonate, disodium 4,41-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-2-triazin-6-ylamino)stilbene-2,21 - disulphonate, disodium 4,41-bis-(4-phenyl-2,1,3-triazol-2-yl)stilbene-2,21 disulphonate, disodium 4,41bis-(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,21 disulphonate and sodium 2(stilbyl-411-(naphtho11,21:4,5)-1,2,3 - triazole-211- sulphonate.

Soil-release agents useful in detergent compositions are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0272033. A particular preferred polymer in accordance with EP-A-0272033 has the formula

\[(\text{CH}_3\text{(PEG)}_{43})_{0.75}\text{(POH)}_{0.25}(\text{T-PO})_{2.8}(\text{T-PEG})_{0.41}(\text{PO-M})_{0.28}(\text{(PEG)}_{43}\text{CH}_3)_{0.75}\]

where PEG is \(-(\text{OC}_2\text{H}_4\text{O})_{\text{n}}\), PO is \((\text{OC}_3\text{H}_6\text{O})\) and T is \((\text{COC}_6\text{H}_4\text{CO})\).

Certain polymeric materials such as polyvinyl pyrrolidones, typically of MWt 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

Another optional detergent composition ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms, exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and
solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartolotta et al. US Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC0544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 5% by weight of the composition, preferably from 0.1% to 3% by weight.

The preferred methods of incorporation comprise either application of the suds suppressors in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation of the suds suppressors into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C₂₀-C₂₄ fatty acids, microcrystalline waxes and high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al US Patent No. 3,933,672.

Another optional ingredient useful in detergent compositions is one or more enzymes. These may be incorporated at a level of from 0.1% to 10%, more preferably 0.5% to 5% by weight of the detergent composition.
Preferred enzymatic materials include the commercially available amylases, neutral and alkaline proteases, lipases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase and Savinase by Novo Industries A/S (Denmark) and Maxatase by International Bio-Synthetics, Inc. (The Netherlands).

Preferred amylases include, for example, -amylases obtained from a special strain of B licheniforms, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, Rapidase, sold by International Bio-Synthetics Inc, and Termamyl, sold by Novo Industries A/S.

An especially preferred lipase enzyme is manufactured and sold by Novo Industries A/S (Denmark) under the trade name Lipolase (Biotechnology Newswatch, 7 March 1988, page 6) and mentioned along with other suitable lipases in EP-A-0258068 (Novo).

A further optional ingredient useful in detergent compositions is a corrosion inhibitor C_{14}-C_{20} fatty acids are preferred examples of such corrosion inhibitors.

Fabric softening agents can also be incorporated into laundry detergent compositions. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Other suitable inorganic softening systems comprising smectite clays, including hectorite and montmorillonite, are also disclosed in EP-A-0522206. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0011340.

Their combination with mono C_{12}-C_{14} quaternary ammonium salts is disclosed in EP-B-0026527 & 528. Other useful organic fabric softening agents are the dilong chain amides as disclosed in EP-B-0242919. Additional

Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight, whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. Where a portion of the composition is spray dried, these materials can be added to the aqueous slurry fed to the spray drying tower, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

In general detergent compositions can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation and preferred methods involve combinations of these techniques. A preferred method of making the granular laundry detergent compositions involves a combination of spray drying, agglomeration in a high speed mixer and dry mixing.

The bulk density of the granular detergent compositions incorporating the bleaching composits of the present invention may be in the range of about 450 to 600 g/litre as is typical for conventional laundry detergent compositions. Alternatively, the granular detergent compositions may be concentrated granular detergent compositions that are characterised by a relatively high density in comparison with conventional detergent compositions. Such high density compositions have a bulk density of at least 650 g/litre, more usually at least 700 g/litre and more preferably from 800 g/litre to 1100 g/litre.

Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a
flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement e.g. a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide the bulk density in g/litre. Replicate measurements are made as required.

Concentrated laundry detergent compositions also normally incorporate at least one multi-ingredient component i.e. they do not comprise compositions formed merely by dry-mixing individual ingredients. Compositions in which each individual ingredient is dry-mixed are generally dusty, slow to dissolve and also tend to cake and develop poor particle flow characteristics in storage.

Preferred laundry detergent compositions comprise at least two particulate multi-ingredient components. The first component comprises at least 15%, conventionally from 25% to 50%, but more preferably no more than 35% by weight of the composition and the second component from 1% to 50%, more preferably 10% to 40% by weight of the composition.

The first component comprises a particulate incorporating an anionic surfactant in an amount of from 0.75% to 40% by weight of the powder and one or more inorganic and/or organic salts in an amount of from 99.25% to 60% by weight of the powder. The particulate can have any suitable form such as granules, flakes, prills, marumes or noodles but is preferably granular. The granules themselves may be agglomerates formed by pan or drum agglomeration or by in-line mixers but are customarily spray dried particles produced by atomising an aqueous slurry of the ingredients in a hot air stream which removes most of
the water. The spray dried granules are then subjected to densification steps, e.g. by high speed cutter mixers and/or compacting mills, to increase density before being reagglomerated. For illustrative purposes, the first component is described hereinafter as a spray dried powder.

Suitable anionic surfactants for the purposes of the first component have been found to be slowly dissolving linear alkyl sulfate salts in which the alkyl group has an average of from 16 to 22 carbon atoms, and linear alkyl carboxylate salts in which the alkyl group has an average of from 16 to 24 carbon atoms. The alkyl groups for both types of surfactant are preferably derived from natural sources such as tallow fat and marine oils.

The level of anionic surfactant in the spray dried powder forming the first component is from 0.75% to 40% by weight, more usually 2.5% to 25% preferably from 3% to 20% and most preferably from 5% to 15% by weight. Water-soluble surfactants such as linear alkyl benzene sulphonates or C_{14-15} alkyl sulphates can be included or alternatively may be applied subsequently to the spray dried powder by spray on.

The other major ingredient of the spray dried powder is one or more inorganic or organic salts that provide the crystalline structure for the granules. The inorganic and/or organic salts may be water-soluble or water-insoluble, the latter type being comprised by the, or the major part of the, water-insoluble builders where these form part of the builder ingredient. Suitable water soluble inorganic salts include the alkali metal carbonates and bicarbonates. Amorphous alkali metal silicates may also be used to provide structure to the spray dried granule provided that aluminosilicate does not form part of the spray dried component.

However, in concentrated detergent compositions it is preferred that no sodium sulphate is added as a separate ingredient and its incorporation as a by-product e.g. with sulph(on)ated surfactants, should be minimised.
Where an aluminosilicate zeolite forms the, or part of the, builder ingredient, it is preferred that it is not added directly by dry-mixing to the other components, but is incorporated into the multi-ingredient component(s).

The first component can also include up to 15% by weight of miscellaneous ingredients such as brighteners, anti-redeposition agents, photoactivated bleaches (such as tetrasulfonated zinc phthalocyanine) and chelants. Where the first component is a spray dried powder it will normally be dried to a moisture content of from 7% to 11% by weight, more preferably from 8% to 10% by weight of the spray dried powder. Moisture contents of powders produced by other processes such as agglomeration may be lower and can be in the range 1-10% by weight.

The particle size of the first component is conventional and preferably not more than 5% by weight should be above 1.4mm, while not more than 10% by weight should be less than 0.15 mm in maximum dimension. Preferably at least 60%, and most preferably at least 80%, by weight of the powder lies between 0.7 mm and 0.25 mm in size. For spray dried powders, the bulk density of the particles from the spray drying tower is conventionally in the range from 540 to 600 g/litre and this is then enhanced by further processing steps such as size reduction in a high speed cutter/mixer followed by compaction. Alternatively, processes other than spray drying may be used to form a high density particulate directly.

A second component of a preferred detergent composition is another multi-ingredient particulate containing a water soluble surfactant.

This may be anionic, nonionic, cationic or semipolar in type or a mixture of any of these. Suitable surfactants are listed hereinbefore but preferred surfactants are C_{14}-C_{15} alkyl sulphates, linear C_{11}-C_{15} alkyl benzene sulphonates and fatty C_{14}-C_{18} methyl ester sulphonates.

The second component may have any suitable physical form, i.e. it may take the form of flakes, prills, marumes, noodles, ribbons, or granules which may be spray-dried or non spray-dried agglomerates. Although the second
component could in theory comprise the water soluble surfactant on its own, in practice at least one organic or inorganic salt is included to facilitate processing. This provides a degree of crystallinity, and hence acceptable flow characteristics, to the particulate and may be any one or more of the organic or inorganic salts present in the first component.

The particle size range of the second component should be such as to obviate segregation from the particles of the first component when blended therewith. Thus not more than 5% by weight should be above 1.4 mm while not more than 10% should be less than 0.15 mm in maximum dimension.

The bulk density of the second component will be a function of its mode of preparation. However, the preferred form of the second component is a mechanically mixed agglomerate which may be made by adding the ingredients dry or with an agglomerating agent to a pan agglomerator, Z blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands and Gebruder Lodige MaschinenbanGmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050 F.R.G. By this means the second component can be given a bulk density in the range from 650 g/litre to 1190 g/litre more preferably from 750 g/litre to 850 g/litre.

Preferred laundry detergent compositions include a level of alkali metal carbonate in the second component corresponding to an amount of from 3% to 15% by weight of the composition, more preferably from 5% to 12% by weight. This will provide a level of carbonate in the second component of from 20% to 40% by weight.

A highly preferred ingredient of the second component is also a hydrated water insoluble aluminosilicate ion exchange material of the synthetic zeolite type, described hereinbefore, present at from 10% to 35% by weight of the second component. The amount of water insoluble aluminosilicate material incorporated in this way is from 1% to 10% by weight of the composition, more preferably from 2% to 8% by weight.
In one process for preparing the second component, the surfactant salt is formed in situ in an inline mixer. The liquid acid form of the surfactant is added to a mixture of particulate anhydrous sodium carbonate and hydrated sodium aluminosilicate in a continuous high speed blender, such as a Lodge C6 mixer, and neutralised to form the surfactant salt whilst maintaining the particulate nature of the mixture. The resultant agglomerated mixture forms the second component which is then added to other components of the product. In a variant of this process, the surfactant salt is pre-neutralised and added as a viscous paste to the mixture of the other ingredients. In the variant, the mixer serves merely to agglomerate the ingredients to form the second component.

In a particularly preferred process for making the granular laundry detergent compositions, part of the spray dried product comprising the first granular component is diverted and subjected to a low level of nonionic surfactant spray on before being reblended with the remainder. The second granular component is made using the preferred process described above. The first and second components together with a crystalline layered silicate particulate composition, the perhydrate bleach and any peroxo acid bleaching precursor particles, other dry mix ingredients such as any carboxylate chelating agent, soil-release polymer and enzyme are then fed to a conveyor belt, from which they are transferred to a horizontally rotating drum in which perfume and silicone suds suppressor are sprayed on to the product. In highly preferred compositions, a further drum mixing step is employed in which a low (approx. 2% by weight) level of finely divided crystalline material is introduced to increase density and improve granular flow characteristics.

In preferred concentrated detergent products incorporating an alkali metal percarbonate as the perhydrate salt it has been found necessary to control several aspects of the product such as its heavy metal ion content and its equilibrium relative humidity. Sodium percarbonate-containing compositions of this type having enhanced stability are disclosed in the commonly assigned British Application No. 9021761.3 filed October 6 1990 (Attorney's Docket No. CM343).
Laundry detergent compositions in accordance with the invention can also benefit from delivery systems that provide transient localised high concentrations of product in the drum of an automatic washing machine at the start of the wash cycle, thereby also avoiding problems associated with loss of product in the pipework or sump of the machine.

Delivery to the drum can most easily be achieved by incorporation of the composition in a bag or container from which it is rapidly releasable at the start of the wash cycle in response to agitation, a rise in temperature or immersion in the wash water in the drum. Alternatively the washing machine itself may be adapted to permit direct addition of the composition to the drum e.g. by a dispensing arrangement in the access door.

Products comprising a laundry detergent composition enclosed in a bag or container are usually designed in such a way that container integrity is maintained in the dry state to prevent egress of the contents when dry, but are adapted for release of the container contents on exposure to a washing environment, normally on immersion in an aqueous solution.

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 fragilble 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.

In a variant of the bag or container form, laminated sheet products can be employed in which a central flexible layer is impregnated and/or coated with a composition 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 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 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.

Suitable materials which can be used for the flexible laminate layers in this aspect of the invention include, among others, sponges, paper and woven and non-woven fabrics.

However the preferred means of carrying a laundry process is to introduce the composition into the liquid surrounding the fabrics that are in the drum via a reusable dispensing device having walls that are permeable to liquid but impermeable to the solid composition.

Devices of this kind are disclosed in European Patent Application Publication Nos. 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.
An article by J. Bland published in Manufacturing Chemist, November 1989, pages 41-46 also describes especially preferred dispensing devices for use with granular laundry detergent products which are of a type commonly known as the "granulette".

The invention is illustrated in the following non-limiting Examples, in which all percentages are on a weight basis unless otherwise stated.
In the detergent compositions, the abbreviated component identifications have the following meanings:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS</td>
<td>Sodium linear C(_{12}) alkyl benzene sulphonate</td>
</tr>
<tr>
<td>TAS</td>
<td>Sodium tallow alkyl sulphate</td>
</tr>
<tr>
<td>TAE(_n)</td>
<td>Tallow alcohol ethoxylated with (n) moles of ethylene oxide per mole of alcohol</td>
</tr>
<tr>
<td>23EY</td>
<td>(Z) C(_{12}-13) primary alcohol condensed with an average of (Y) moles of ethylene oxide</td>
</tr>
<tr>
<td>25EY</td>
<td>A C(_{12}-15) predominantly linear primary alcohol condensed with an average of (Y) moles of ethylene oxide</td>
</tr>
<tr>
<td>45EY</td>
<td>A C(_{14}-15) predominantly branched primary alcohol condensed with an average of (Y) moles of ethylene oxide</td>
</tr>
<tr>
<td>TAED</td>
<td>Tetraacetyl ethylene diamine</td>
</tr>
<tr>
<td>Silicate</td>
<td>Amorphous Sodium Silicate (SiO(_2):Na(_2)O ratio normally follows)</td>
</tr>
<tr>
<td>NaSKS-6</td>
<td>Crystalline layered silicate of formula (\delta)-Na(_2)Si(_2)O(_5)</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Anhydrous sodium carbonate</td>
</tr>
<tr>
<td>CMC</td>
<td>Sodium carboxymethyl cellulose</td>
</tr>
</tbody>
</table>
Zeolite A : Hydrated Sodium Aluminosilicate of formula Na_{12}(AlO_2SiO_2)_{12}. 27H_2O having a primary particle size in the range from 1 to 10 micrometers

Polyacrylate : Homopolymer of acrylic acid of MWt 4000

Citrate : Tri-sodium citrate dihydrate

MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000.

Perborate : Anhydrous sodium perborate monohydrate bleach, empirical formula NaBO_2.H_2O_2

PB4 : Anhydrous sodium percarbonate tetrahydrate bleach, empirical formula NaBO_2H_2O_2 . 3H_2O

Enzyme : Mixed proteolytic and amylolytic enzyme sold by Novo Industries AS.

DETPMP : Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060

Suds : 25% paraffin wax Mpt 50°C, 17% hydrophobic silica, 58% paraffin oil.

Suppressor : Ethylenediamine-N,N'-disuccinic acid (S,S isomer)

Sulphate : Anhydrous sodium sulphate.

EDTA : Ethylene diamine tetra acetate.
Amylase : Amylolytic enzyme sold by Novo Industries A/S under the tradename Termamyl.
Protease : Proteolytic enzyme sold by Novo Industries A/S under the tradename Savinase.

NaCl : Anhydrous sodium chloride

Nonionic: A C13-C15 ethoxylated/propoxylated fatty alcohol with a degree of ethoxylation of 3.8 and a degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF GmbH.

Montmorillonite : A smectite-type clay softening agent
Hectorite : A smectite-type clay softening agent
CAS : Sodium coconut alkyl sulfate
PEPA : Poly ethyl propoxy alcohol
Sulphuric : Sulphuric acid
Example 1

The following peroxy bleach containing laundry detergent products were prepared (parts by weight). Products A and B are prior art compositions and products C and D are in accordance with the invention.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tbody>
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</tr>
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<td>5.0</td>
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<td>-</td>
<td>-</td>
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<td>0.4</td>
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<td>-</td>
</tr>
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<td>-</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
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<td>0.5</td>
</tr>
<tr>
<td>Suds Suppressor</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Enzyme</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Silicate (2.0 ratio)</td>
<td>4.4</td>
<td>4.4</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>MgSO4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Sulphate</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Water and miscellaneous to balance
A beaker containing 1000 ml of water of 17° German Hardness (243 ppm CaCO3) was placed in a constant temperature bath set at 90°C and allowed to reach the bath temperature. To this beaker was added heavy metal ions in the form of a soluble, inert inorganic salt to give a heavy metal ion concentration by weight of 1.1 ppm Cu, 2 ppm Fe, 2.3 ppm Zn and 0.12 ppm Mn. These levels of Cu, Fe, Zn and Mn are believed to be representative of the levels which may be found in the wash liquor of an automatic washing machine when a typical load of soiled laundry is being washed. To the beaker was added one of the detergent products at a level of 0.7% detergent product by weight of the solution. Aliquots of the solution were removed from the beaker at fixed time intervals and the % H2O2 (from the perborate bleach) remaining determined as a percentage of the amount present in the detergent product before its addition to the solution. The % H2O2 remaining was determined by discharging the aliquot into 20% sulfuric acid solution, which prevents any further decomposition of the H2O2, and then performing the standard permanganate titration with 0.1N KMnO4. The identical procedure was used for each of the products A, B, C and D. Replicates were performed until consistent results were obtained.

Presented below is the % H2O2 remaining at fixed time intervals from the time of addition of the detergent product to the beaker for each of the products A, B, C and D.

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>% H2O2 Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>92.6</td>
</tr>
<tr>
<td>10</td>
<td>82.6</td>
</tr>
<tr>
<td>20</td>
<td>67.4</td>
</tr>
<tr>
<td>30</td>
<td>47.4</td>
</tr>
<tr>
<td>50</td>
<td>29.0</td>
</tr>
</tbody>
</table>

The comparison of the results shows that the EDTA containing composition A gives significantly worse bleach stabilization than either the phosphonate
containing composition B, or the EDDS containing compositions C and D. EDDS is seen to give comparable bleach stabilization to DETPMP both when used on an equal weight (0.4%) and equimolar (0.2%) basis to the phosphonate chelant.

Example 2

The following machine dishwashing detergent compositions were prepared (parts by weight). Products E and F are prior art compositions and product G is in accordance with the invention.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate</td>
<td>42.4</td>
<td>42.4</td>
<td>42.4</td>
</tr>
<tr>
<td>MA/AA</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Silicate (2.0 ratio)</td>
<td>33.0</td>
<td>33.0</td>
<td>33.0</td>
</tr>
<tr>
<td>Nonionic</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Perborate</td>
<td>10.4</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>TAED</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Amylase</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Protease</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>EDTA</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DETPMP</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>EDDS</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Moisture/Miscellaneous to balance

A similar procedure was used to the test described in Example 1 but adjustments were made to make the test more representative of domestic automatic dishwashing process conditions. A beaker containing 1000 ml water of 17° German Hardness (243 ppm CaCO₃) was placed in a constant temperature bath initially set at 20°C. To this beaker was added heavy metal ions in the form of inert, soluble inorganic salts to give a heavy metal ion concentration by weight of 1.5 ppm Cu and 0.67 ppm Fe. These levels of Cu and Fe are believed to be typical of the levels which might be found in the wash liquor of a domestic automatic dishwashing machine during a typical
wash cycle with a normal wash load. To the beaker was added one of the detergent products to give a level of 0.4% detergent product by weight of the solution. The solution was heated at a constant rate such that after 15 minutes the solution temperature reached 65°C at which time an aliquot of solution was removed and the % H₂O₂ remaining determined as herinbefore described.

The solution was then maintained at a temperature of 65°C for a further 10 minutes at which time a second aliquot of solution was removed and the % H₂O₂ remaining similarly determined. Replicates were performed until consistent results were obtained. The % H₂O₂ remaining for each of the products E, F and G is given below.

<table>
<thead>
<tr>
<th>%H₂O₂ Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (Minutes)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>25</td>
</tr>
</tbody>
</table>
**Example 3**

The following peroxy bleach containing laundry detergent products containing smectite clay type softening agents were prepared in accordance with the invention.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>TAS</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>45E7</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>19.5</td>
<td>19.5</td>
</tr>
<tr>
<td>Citrate</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>MA/AA</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Carbonate</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Perborate</td>
<td>5.8</td>
<td>5.8</td>
</tr>
<tr>
<td>PB4</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>TAED</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>EDDS</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>CMC</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>Suds Suppressor</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Enzyme</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Silicate (2.0 ratio)</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>MgSO4</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>Sulphate</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>12.5</td>
<td>-</td>
</tr>
<tr>
<td>Hectorite</td>
<td>-</td>
<td>12.5</td>
</tr>
</tbody>
</table>

*Water, minors and miscellaneous to balance*
Example 4

The following liquid peroxy bleach containing formulations, suitable for use as household cleaners or as bleach additives, were prepared in accordance with the invention:

<table>
<thead>
<tr>
<th></th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide</td>
<td>8.50</td>
<td>3.5</td>
</tr>
<tr>
<td>CAS</td>
<td>0.8</td>
<td>12.0</td>
</tr>
<tr>
<td>PEPA</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>23E3</td>
<td>-</td>
<td>1.8</td>
</tr>
<tr>
<td>Sulphonic</td>
<td>up to pH4</td>
<td>-</td>
</tr>
<tr>
<td>Manoethanol amine</td>
<td>-</td>
<td>up to pH2.5</td>
</tr>
<tr>
<td>EDDS</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Water and minors</td>
<td>up to 100</td>
<td>up to 100</td>
</tr>
</tbody>
</table>

Minors include perfume, brightener and dye
Claims

1. A bleaching composition comprising:
   
   (a) a peroxy compound, selected from hydrogen peroxide and the addition compounds of hydrogen peroxide, organic per oxyacids, and mixtures thereof; and
   
   (b) from 0.05% to 2% by weight of the composition of ethylenediamine-N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substituted ammonium salts thereof, or mixtures thereof,

   wherein the weight ratio of said peroxy compound to said ethylenediamine-N,N'-disuccinic acid lies in the range from 800 : 1 to 10 : 1.

2. A bleaching composition according to Claim 1 wherein the ethylenediamine-N,N'-disuccinic acid is in the form of its [S,S] isomer.

3. A bleaching composition according to either Claims 1 or 2 wherein the ethylenediamine-N,N'-disuccinic acid component is present at a level of from 0.05% to 1% by weight of the composition and wherein said weight ratio is from 400:1 to 20:1.

4. A bleaching composition according to any of Claims 1 - 3 wherein the ethylenediamine-N,N'-disuccinic acid component is present at a level of from 0.1% to 0.5% by weight of the composition and wherein said weight ratio is from 200:1 to 40:1.

5. A bleaching composition according to any of Claims 1-4 incorporating per oxyacid bleach precursor.

6. A bleaching composition useful in the bleaching of cellulosic fibre and synthetic textiles according to any of Claims 1-5 wherein the peroxy compound is hydrogen peroxide.
7. A bleaching composition according to Claim 6 wherein the bleaching composition contains no sodium silicate.

8. A detergent composition comprising a bleaching composition according to any of Claims 1-5 wherein said peroxo compound is an inorganic perhydrate salt, and is present at levels from 3% to 40% by weight of the detergent composition and wherein said detergent composition further comprises from 1% to 80% by weight of the detergent composition of non-phosphate detergent builder compounds, and mixtures thereof.

9. A detergent composition according to Claim 8 wherein the ethylenediamine-N,N\(^1\)-disuccinic acid component is in the form of a magnesium salt.

10. A machine dishwashing detergent composition according to either Claim 8 or 9 incorporating from 0.5% to 10% by weight of low foaming surfactant selected from anionic, cationic, nonionic, ampholytic and zwitterionic surfactants, and mixtures thereof.

11. A machine dishwashing detergent composition according to Claim 10 incorporating enzyme selected from amylolytic, proteolytic and lipolytic enzymes and mixtures thereof.

12. A laundry detergent composition according to either one of Claims 8 or 9 comprising from 3% to 30% by weight of surfactant, selected from anionic, cationic, nonionic, ampholytic and zwitterionic surfactants, and mixtures thereof.

13. A laundry detergent composition according to Claim 12 wherein the non-phosphate detergent builder compounds are selected from crystalline layered sodium silicates, sodium aluminosilicate zeolites, alkali metal carbonates and bicarbonates, carboxylates and polycarboxylates, and maleic anhydride / acrylic acid copolymers.
14. A laundry detergent composition according to Claim 13 wherein the crystalline layered sodium silicate detergent builder compound is a material of formula $NaMSi_{x}O_{2x+y}H_{2}O$ wherein $M$ is sodium or hydrogen, $x$ is a number from 1.9 to 4 and $y$ is a number from 0 to 20.

15. A laundry detergent composition according to any of Claims 12-14 wherein the crystalline layered silicate material is $\alpha$-Na$_2$Si$_2$O$_5$ (Na SKS-6).

16. A laundry detergent composition according to any of Claims 12-15 wherein the anionic surfactant comprises a mixture of a C$_{12-20}$ alkyl sulfate salt with a water soluble C$_{11-19}$ alkyl ethoxysulfate salt containing an average of from 1 to 7 ethoxy groups per mole wherein the weight ratio of said alkyl sulfate salt to said alkyl ethoxysulfate salt lies in the range from 2 : 1 to 19 : 1.

17. A laundry detergent composition according to Claim 16 wherein the alkyl sulfate salt is a C$_{14-15}$ alkyl sulfate salt, the alkyl ethoxysulfate salt is a C$_{12-15}$ alkyl ethoxysulfate salt containing an average of three ethoxy groups per mole and wherein said weight ratio lies in the range from 3.5 : 1 to 10 : 1.

18. A laundry detergent composition according to any of Claims 12-17 wherein the nonionic surfactant is a polyhydroxy fatty acid amide of formula

$$\begin{align*}
O & \quad R^1 \\
\mid \quad \mid \\
R^2 & \quad C \quad N \quad CH_2(CHOH)_4CH_2OH
\end{align*}$$

where $R^1$ is H, C$_{1-4}$ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl or a mixture thereof, $R^2$ is C$_{5-31}$ hydrocarbyl and $Z$ is a poly hydroxyhydrocarbyl having a linear hydrocarbon chain with at least 3
hydroxy groups directly connected to said chain, or an alkoxylated derivative thereof.

19. A laundry detergent composition according to any of Claims 12-18 wherein the nonionic surfactant is a C9-C15 primary alcohol ethoxylate containing an average of from 3 to 8 moles of ethylene oxide per mole of alcohol.

20. A laundry detergent composition according to Claim 19 wherein the primary alcohol ethoxylate is C12-C15 primary alcohol containing an average of from 3 to 5 moles of ethylene oxide per mole of alcohol.

21. A laundry detergent composition according to any of Claims 12-20 incorporating from 1% to 20% by weight of a solid peroxycacid bleach precursor.

22. A laundry detergent composition according to Claim 21 wherein the inorganic perhydrate salt is sodium percarbonate present at a level of from 5% to 30% by weight and the solid peroxycacid bleach precursor is TAED present at a level of from 1% to 10% by weight of the composition.

23. A laundry detergent composition according to any of Claims 12-22 comprising additional detergent components selected from detergent enzymes, soil suspension and anti-redeposition agents, optical brighteners, suds suppressors, perfumes and mixtures thereof.

24. A composition comprising a bleaching composition according to any of Claims 1-5 wherein said composition is liquid and wherein the per oxy compound is selected from hydrogen peroxide, organic peroxyacids, and mixtures thereof and wherein the composition has a pH of from 0.5 to 6.

25. A composition according to claim 24 wherein the per oxy compound is dissolved or dispersed in the liquid composition or is incorporated as an emulsion or suspension.
26. A composition according to either of Claims 24 or 25 incorporating peroxyacid bleach precursor wherein said peroxyacid bleach precursor is dissolved or dispersed in the liquid or is incorporated as an emulsion or suspension.

27. A composition according to any of Claims 24-26 wherein said composition is formulated as a hard surface-cleaner, or as a laundry additive, or as a stain pretreatment composition, or as a carpet or upholstery cleaner.
A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C09K 1/520; C11D 3/03, 3/39, 3/395, 7/54; D06L 3/02
US CL : Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/111, 137; 252/102, 186.29, 186.31 403, 527, 546; 523/279, 415P, 584

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US,A, 3,049,495 (Jenkins) 14 August 1962</td>
<td>1-3</td>
</tr>
<tr>
<td>Y</td>
<td>US,A, 3,686,126 (Smeets) 22 August 1972 see Col. 2, lines 26-47.</td>
<td>1-3</td>
</tr>
<tr>
<td>Y</td>
<td>US,A, 4,075,116 (Mesaros) 21 February 1978 see Col. 2, lines 1-11.</td>
<td>1-3</td>
</tr>
<tr>
<td>A</td>
<td>US,A, 4,378,300 (Gray) 29 March 1983</td>
<td>1-3</td>
</tr>
<tr>
<td>Y</td>
<td>US,A, 4,704,233 (Hartman et al) 03 November 1987 see Col. 9, lines 3-16 &amp; Col. 14, lines 11-23</td>
<td>1-3</td>
</tr>
</tbody>
</table>

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be part of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclaimer, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"Z" member of the same patent family

Date of the actual completion of the international search: 15 SEPTEMBER 1993
Date of mailing of the international search report: 15 OCT 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer: DENNIS L. ALBRECHT
Telephone No.: (703) 308-2525

Facsimile No.: NOT APPLICABLE

Form PCT/ISA/210 (second sheet)(July 1992)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>US, A, 4,737,306 (Wichelhaus) 12 April 1988 See Col. 11, lines 50-56; Col. 14, line 63-Col. 15, line 21 and EXAMPLES 15-3 &amp; 15-4.</td>
<td>1-3</td>
</tr>
</tbody>
</table>
A. CLASSIFICATION OF SUBJECT MATTER:

US CL:

8/111, 137; 252/102, 186.29, 186.31, 403, 527, 546; 523/279, 415P, 584
Box I  Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-27 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II  Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest  □ The additional search fees were accompanied by the applicant’s protest.
□ No protest accompanied the payment of additional search fees.