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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

There is provided a detergent composition comprising alkali metal percarbonate and alkyl polysaccharide surfactant which gives improved overall performance, in particular removal of greasy stains, over compositions comprising perborate and alkyl polysaccharide. There is also provided a low temperature washing process in which the composition of the invention is a laundry detergent composition and is introduced into the wash liquor during the wash. Such a process is particularly effective when the laundry comprises hydrophobic material such as polyester and polycotton.

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DETERGENT COMPOSITIONS

This invention relates to detergent compositions, in particular laundry detergent compositions comprising alkyl polysaccharide surfactants. The laundry detergent compositions are particularly suitable for use in a low temperature process for washing laundry in a domestic washing machine.

Grease and oil cleaning performance is one important attribute of many, if not most, detergent compositions. Linear alkyl benzene sulphonates have traditionally been utilised in detergent compositions for their superior grease/oil and good overall cleaning ability over a wide variety of wash conditions. Whereas linear alkyl benzene sulphonates have performed admirably, they tend to be largely petroleum-derived surfactants. Thus, it is desirable to decrease the level of these and other petroleum-derived surfactants and replace them with surfactants that typically are primarily derived from renewable resources, so long as excellent overall cleaning, including grease and oil removal, could be maintained.

It is known to incorporate alkyl polysaccharide, in particular alkyl polyglucoside, surfactants into detergent compositions to proportionally reduce the level of, or eliminate, linear alkyl benzene sulphonate and other petroleum-derived surfactants. Excellent overall cleaning, including grease and oil cleaning, over a wide variety of conditions is preserved. The use of alkyl polysaccharide surfactants in laundry detergent composition is described in, for instance, EP-A-0,075,994 and EP-A-0,075,995. Their use for a variety of purposes is described in EP 70074.

It is known to provide detergent compositions incorporating an inorganic perhydrate salt as a source of oxygen bleach. The inorganic perhydrate bleach most widely used in detergent compositions is sodium perborate in the form of either the monohydrate or the tetrahydrate. It is believed that on dissolution in water, perborate gives borate ions and that these borate ions are capable of forming ionic complexes with α(vicinal) diols such as alkyl polysaccharides. Such ionic complexes have increased solubility and hydrophilicity over the non-complexed alkyl polysaccharide and so their interaction with and removal of grease and oil is altered and this can be undesirable. It can reduce performance.

This problem is particularly noticeable when the detergent composition contains, relative to the amount of polysaccharide, a large proportion of perborate or a large proportion of anionic surfactant.

According to the invention there is provided a detergent composition comprising:

(a) alkali metal percarbonate

and

(b) one or more alkyl polysaccharides of formula

$$RO(C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from a saccharose; R is a saturated hydrophobic alkyl group that contains from 8 to 20 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 10.

The detergent composition of the invention may take various forms; it may be for instance a machine dishwashing composition, a hand dishwashing composition or, in particular, a laundry detergent composition.

According to the invention there is also provided a process of washing laundry, preferably in a domestic washing machine, in which an effective amount of a laundry detergent composition of the invention is introduced into the wash liquor during the wash, wherein the process is conducted at a temperature of no more than 50°C. The alkyl polysaccharide preferably remains substantially unionised during the wash.

The process is preferably conducted at a temperature of no more than 45°C, more preferably of no more than 40°C, most preferably of between 10 and 35°C. The process of the invention is particularly effective when the laundry comprises hydrophobic fabrics such as polyester and polycotton.

During the wash a certain minor amount of ionisation may occur naturally as the alkylpolysaccharide interacts with water. However this, if it occurs, will only do so to a minor degree. Ionisation of the kind believed to occur in perborate-containing compositions does not occur in the compositions of the invention.

It has been found that the detergent compositions comprising percarbonate and alkyl polysaccharides give superior grease and oil removal performance over detergent compositions comprising perborate and alkyl polysaccharides. It seems that percarbonate does not hinder the interaction of alkyl polysaccharides with the components of stains. This is probably due to the percarbonate not causing ionisation of the diol moiety in the alkyl polysaccharide molecules. Irrespective of the mechanism, it is surprisingly possible to achieve better greasy stain removal properties and overall cleaning performance of alkyl polysaccharides by using percarbonate instead of perborate.

Performance is also enhanced when used for other washing purposes, e.g. of dishes.

The alkyl polysaccharides have a general formula $RO(C_nH_{2n}O)_tZ_x$. Z is a moiety derived from a saccharose, for instance galactoside, glucoside, fructoside, glucosyl, fructosyl, galactosyl. Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants.

R is a hydrophobic group containing from 8 to 20 carbon atoms, preferably from 10 or 12 to 18 carbon atoms, most preferably from 12 to 14 carbon atoms.

R is preferably a linear alkyl group. It may contain up to 3 hydroxy groups. Suitable alkyl groups are octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, hextadecyl and octadecyl.

Preferred materials are alkyl polyglucosides wherein the alkyl group contains 8 to 18, preferably 12 to 18, carbon atoms and x is up to 4,preferably about 1.2 to about 2.7, more preferably about 1.2 to about 2, most preferably about 1.5 to about 2.

The group R can be attached at the 2-, 3- or 4-position rather at the 1-position (thus giving for instance a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the one-position, i.e., glucosides, galactosides, fructosides, etc. is preferred. In preferred alkyl polysaccharides the additional saccharide units are predominantly attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6-positions can also occur.

The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule, x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will in general be molecules having different x values. The physical sample can be characterised by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. X preferably has a value from about 1.1 to about 4, preferably about 1.2 to about 2.7, more preferably from about 1.2 to about 2.

Optionally there can be a polyalkoxide chain $(C_nH_{2n}O)_t$ joining the hydrophobic alkyl group of R and the polysaccharide chain. Most preferably t is 0; when however t is above 0 n may be 2 or 3, preferably 2, giving an ethoxide moiety.

As used herein, "alkylpolysaccharide" is intended to represent both the preferred glucose derived surfactants and the less preferred alkylpolysaccharide surfactants. Throughout this specification, "alkylpolysaccharide" is used to include alkylpolyglucosides because the stereo chemistry of the saccharide moiety is changed during the preparation reaction.

The alkali metal percarbonate used is preferably sodium or potassium percarbonate, more preferably sodium percarbonate. The percarbonate is generally in particulate form. The percarbonate particles generally have a mean particle diameter of 150 to 1200 µm, preferably 300 to 900µm. The particles of percarbonate may be coated or uncoated. If they are coated this is preferably with a water-soluble coating. Suitable coating materials include the alkali or alkaline earth metal carbonates; the alkali or alkaline earth metal sulphates; the mixed salts of alkali or alkaline earth metal sulphates and carbonates; the mixed salts of alkali or alkaline earth metal chlorides and carbonates; the mixed salts of alkali or alkaline earth metal nitrates and carbonates. Suitable coatings together with coating processes have been described in GB 1,466,799.

The percarbonate may be present in the detergent composition in any of the proportions used conventionally. The benefits of the invention are shown in particular by compositions containing a large proportion of oxygen-releasing bleaching agent, for instance 9% or more by weight. Since it has been found that it is advantageous to replace perborate with percarbonate and that hindrance of performance is particularly noticeable in compositions containing high proportions of perborate, the benefits of the invention will be felt in particular in equivalent formulations containing percarbonate. Thus the advantages of the invention are most noticeable in compositions containing percarbonate in an amount of 9% or more by weight of total composition.

Stain removal and other performance characteristics of alkyl polysaccharides in the presence of perborate are particularly hindered in the presence of high levels of anionic surfactant, for instance when the ratio of the weight of the anionic surfactant to the weight of the one or more alkyl polysaccharides is one or greater. Therefore the benefits of the invention are shown particularly in equivalent formulations containing percarbonate wherein the ratio of anionic surfactant to alkyl polysaccharide is at least 1, preferably at least 1.5, up to 10 or more. Preferred anionic surfactants are alkyl sulphates, in particular alkyl sulphates having from 12 to 22, preferably 6 to 18, carbon atoms in the alkyl radical. A particularly useful surfactant system comprises a mixture of 2 alkyl sulphate materials whose respective mean chain lengths differ from each other. When such a system comprises a mixture of C_{14} to C_{15} alkyl sulphate and C_{16} to C_{18} alkyl sulphate in a weight ratio of C_{14} to C_{15}:C_{16} to C_{18} of from 3:1 to 1:1.

Other surfactants conventionally used in detergent compositions may be included in the compositions of the invention as desired. Suitable additional surfactants are described below.

It may be found useful to include detergent builder at a high level, for instance greater than 30%. Suitable builders include aluminosilicate ion exchange materials, in particular zeolites, citrates, crystalline layered sodium silicates, in particular NaSKS-6 (available from Hoechst AG FRG), alkali metal carbonates and bicarbonates, amorphous silicates and STPP. Other conventional detergent builders may be used as desired. Builder systems are described in more detail below.

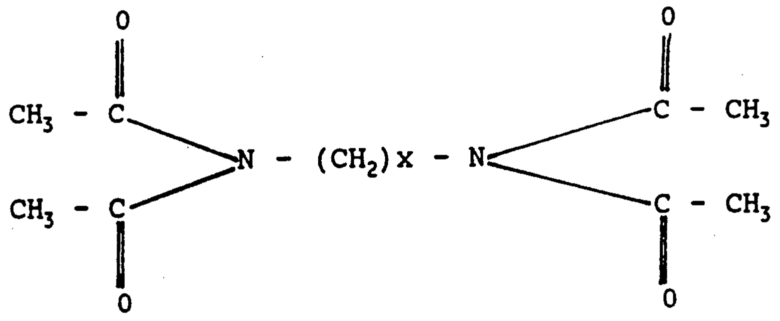
The total amount of surfactant, including alkyl polysaccharide and anionic surfactant if any, may range from 3 to 35%, preferably from 10 to 25%, by weight of total composition.

The compositions of the invention may also include from 1 to 20% by weight of total composition, preferably from 2 to 15% by weight, most preferably from 3 to 10% by weight of additional bleaching agents selected from peroxyacid bleach precursors and organic peroxyacids and mixtures thereof. Such additional bleaching agents are described in further detail below.

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 precursors (bleach activators) and preformed organic peracids.

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.

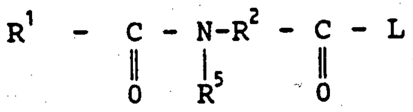
Particularly preferred precursor compounds are the N,N,N^1,N^1 tetra acetylated compounds of formula



wherein x can be 0 or an integer between 1 & 6.

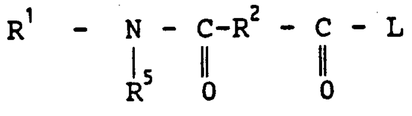
Examples include tetra acetyl methylene diamine (TAMD) in which x=1, tetra acetyl ethylene diamine (TAED) in which x=2 and tetra acetyl hexylene diamine (TAHD) in which x=6. These and analogous compounds are described in GB-A-907356. The most preferred peroxyacid bleach precursor is TAED.

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



$R^1 - \underset{\underset{O}{\|}}{C} - \underset{\underset{R^5}{|}}{N}-R^2 - \underset{\underset{O}{\|}}{C} - L$

or

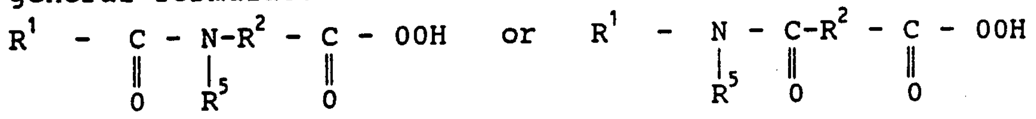


$R^1 - \underset{\underset{R^5}{|}}{N} - \underset{\underset{O}{\|}}{C}-R^2 - \underset{\underset{O}{\|}}{C} - L$

wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, or alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 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. The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Other peroxyacid bleach precursor compounds include sodium nonanoyloxy benzene sulfonate, sodium trimethyl hexanoyloxy benzene sulfonate, sodium acetoxy benzene sulfonate and sodium benzoyloxy benzene sulfonate as disclosed in, for example, EP-A-0341947.

The compositions of the invention may contain as a peroxy compound organic peroxyacids of which a particularly preferred class are the amide substituted peroxyacids of general formulae:



$$R^1-\underset{\underset{O}{\|}}{C}-\underset{\underset{R^5}{|}}{N}-R^2-\underset{\underset{O}{\|}}{C}-OOH \quad \text{or} \quad R^1-\underset{\underset{R^5}{|}}{N}-\underset{\underset{O}{\|}}{C}-R^2-\underset{\underset{O}{\|}}{C}-OOH$$

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 dicacyl peroxides and dialkyl peroxides. Suitable are diperoxy dodecanedioc acid, diperoxy tetra decanedioc acid, diperoxyhexadecanedioc acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

The detergent compositions of the invention 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 hand or automatic dishwashing processes, as laundry additive compositions, denture care formulations, 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.

The detergent compositions may in addition comprise in general terms those ingredients commonly found in detergent products which may include further organic surfactants, detergent builders, anti-redeposition and soil suspension 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 in addition to alkyl polysaccharides. 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 C_{14}-C_{15} alkyl sulfate salts, that is where the degree of branching of the C_{14}-C_{15} alkyl chain is greater than about 20%. Such substantially branched C_{14}-C_{15} alkyl sulfate salts are usually derived from synthetic sources. Also preferred are

C_{16}-C_{20} alkyl sulfate salts which are usually derived from natural sources such as tallow fat and marine oils.

The C_{11}-C_{18} alkyl ethoxysulfate salt comprises a primary alkyl ethoxysulfate which is derived from the condensation product of a C_{11}-C_{18} alcohol condensed with an average of from one to seven ethylene oxide groups, per mole. Preferred are the C_{12}-C_{15} 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.

The C_{11}.C_{18} alcohol itself can be obtained from natural or synthetic sources. Thus, C_{11}-C_{18} 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 Dobanol 25 (RTM) sold by Shell Chemicals (UK) Ltd which is a blend of C_{12}-C_{15} alcohols, Ethyl 24 sold by the Ethyl Corporation, a blend of C_{13}.C_{15} alcohols in the ratio 67% C_{13}, 33% C_{15} 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 C_{11}-C_{18} 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

$$R\text{-}CON\ (R^1)\ CH_2\ COOM$$

wherin R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and 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 preferred nonionic surfactant is a polyhydroxy fatty acid amide surfactant compound having the structural formula:

$$R^2 - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle R^1}{|}}{N} - Z$$

wherein: R^1 is H, C_1-C_4 hydrocarbyl, 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} hydrocarbyl, 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 polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxlylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. 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 $-CH_2-(CHOH)n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, 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 glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

R^2-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-triotityl, etc. Preferred compound are N-methyl N-1deoxyglucityl C_{14}-C_{18} fatty acid amides.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_6C_{20}, preferably C_{10}-C_{14} N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxpropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_8-C_{16}, preferably C_{10}-C_{14} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Laundry detergent compositions incorporating the detergent compositions of the invention comprise from 3% to 35% of surfactant but more usually comprise from 5% to 25%, more preferably from 10% to 25% surfactant by weight of the compositions.

Machine dishwashing detergent compositions incorporating the detergent 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, amphoteric 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 C_6-C_{16} fatty alcohols and C_6-C_{16} mixed ethoxylated/propoxylated fatty alcohols and mixtures thereof. Preferably, the ethoxylated fatty alcohols are the C_{10}-C_{16} ethoxylated fatty alcohols with a degree of ethoxylation of from 5 to 50, most preferably these are the C_{12}-C_{16} 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

$$NaMSi_xO_{2x+1}.yH_2O$$

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 $Na_2Si_2O_5$. 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 -$Na_2Si_2O_5$, 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 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 5% 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, such as zeolites A, B, HS, X, Y, P and MAP and mixtures thereof, preferred sodium aluminosilicate zeolites have the unit cell formula

$$Na_z\ [(AlO_2)_z\ (SiO_2)_y]\ xH_2O$$

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 $CaCO_3$ 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 $CaCO_3$/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 $CaCO_3$/litre/minute/(gram/litre) [2 grains/gallon/minute/ (gram/gallon)] to 390 mg equivalent of $CaCO_3$/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 $CaCO_3$/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 exchange materials is discussed in US Patent No. 3,985,669. Preferred 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

$$Na_{12}\ [(AlO_2)_{12}\ (SiO_2)_{12}\ ].\ xH_2O$$

wherein x is from 20 to 30, especially 27. Zeolite X of formula $Na_{86}\ [(AlO_2)_{86}(SiO_2)_{106}].\ 276\ H_2O$ is also suitable, as well as Zeolite HS of formula $Na_6\ [(AlO_2)_6(SiO_2)_6]\ 7.5\ H_2O)$.

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 (pK_1) 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

$$H^+ + A^- \rightleftharpoons HA$$

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

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

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

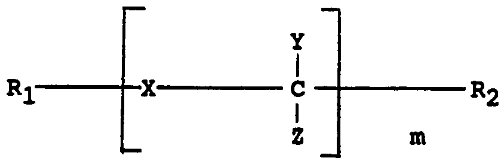
and $pK_1 = \log_{10}K$.

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 momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance

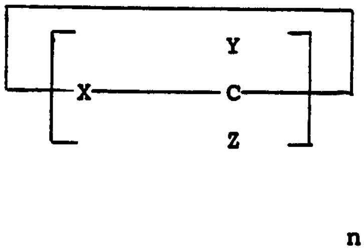
Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates having the general formulae

(a)



$$R_1-\left[X-\overset{Y}{\underset{Z}{C}}\right]_m-R_2$$

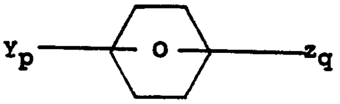
(b)



$$\left[X-\overset{Y}{\underset{Z}{C}}\right]_n \text{ (cyclic)}$$

or

(c)



wherein R_1 represents H,C_{1-30} alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethylenoxy 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, (ethylenedioxy) 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, lactoxysuccinates 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 detergent 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 tremethylene 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 the automatic dishwashing detergent compositions of the present invention. Suitable silicates include the water soluble sodium silicates with an SiO_2 : Na_2O 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_2O 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 $SiO_2:Na_2O$ ratio in the range from 1.6 to 3.4, ratios from 2.0 to 2.8 being preferred.

The detergent 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 peroxyacids 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 hydroxyethycellulose, 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 4,4^{1}-bis-(2-diethanolamino-4-anilino -s- triazin-6- ylamino)stilbene-2:2^{1} disulphonate, disodium 4,4^{1}-bis-(2-morpholino -4-anilino-2-triazin-6-ylaminostilbene-2:2^{1}-disulphonate,disodium 4, 4^{1}-bis-(2,4-dianilino-s-triazin-6-ylamino)st ilbene-2:2^{1} - disulphonate, monosodium 4^{1},4^{11}-bis-(2,4-dianilino-s-triazin-6-ylam ino)stilbene-2-sulphonate, disodium 4,4^{1}-bis-(2-anilino-4-(N-methyl-N-2-hydroxye thylamino)-2-triazin-6-ylamino)stilbene-2,2^{1} -disulphonate, disodium 4,4^{1}-bis-(4-phenyl-2,1,3-triazol-2-yl)stilbe ne-2,2^{1} disulphonate, disodium 4,4^{1}bis(2-anilino-4-(1-methyl-2-hydroxyethyl amino)-s-triazin-6-ylamino)stilbene-2,2^{1}disulp honate and sodium 2(stilbyl-4^{11}-(naphtho-1^{1},2^{1}:4,5)-1,2,3 - triazole-2^{11}- 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

$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\text{-}H)_{0.25}((PEG)_{43}CH_3)_{0.75}$ where PEG is $-(OC_2H_4)O-$,PO is (OC_3H_6O) and T is $(pCOC_6H_4CO)$.

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 m^2/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 Bartollota et al. US Patent 3,933,672. Other particularly useful suds suppressors are the selfemulsifying 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 C_{20}-C_{24} 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 compostions 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 examplified 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 organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0299575 and 0313146.

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 compositons 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 cylindricl 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 lease 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}-C_{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 Lodige 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 peroxy acid bleach 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.

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 frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

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 sufficent 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".

A laundry detergent composition of the invention is illustrated in the following non limiting Example, in which all percentages are on a weight basis unless otherwise stated.

In the detergent compositions, the abbreviated component identifications have the following meanings:

C_{14-15}AS : Sodium C_{14}-C_{15} alkyl sulphate

25E3S : Sodium C_{12}-C_{15} alkyl sulphate condensed with an average of 3 moles of ethylene oxide per mole

C_{14-15}AE7 : a C_{14}-C_{15} primary alcohol condensed with an average of 7 moles of ethylene oxide per mole

C_{12-14} APG (x=1.4) : C_{12}-C_{14} alkyl polyglucoside. Degree of glucosidation x=1.4

TAED : Tetraacetyl ethylene diamine

NaSKS-6 : Crystalline layered silicate of formula $\delta - Na_2Si_2O_5$

CMC : Sodium carboxymethyl cellulose

Zeolite 4A : 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

Citrate : Tri-sodium citrate dihydrate

MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000, available from BASF under the tradename Sokalan CP5.

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

Suds Suppressor : a mixture of silicone oil and hydrophobic silica

Savinase : Proteolytic enzyme sold by Novo Industries A/S

Percarbonate : Anhydrous sodium percarbonate bleach of empirical formula $2Na_2CO_3.3H_2O_2$

The following is an example of a laundry detergent composition according to the invention:

C14-15 AS	9%
25E3S	2.5%
C14-15 AE7	1.0%
C12-14 APG (x=1.4)	3.0%
Suds Supressor	1.0%
Zeolite A	20.0%
NaSKS-6 (Layered Silicate 2.0 Ratio)	10.0%
Citrate	3.0%
Copolymer AA/MA	2.0%
Sodium Carbonate (anhydrous)	10.0%
Percarbonate	20.0%
TAED	5.0
Savinase (4.0 KNPU/g)	1.5%
CMC	0.5%
Phosphonate (DTPMP)	0.5%
Balance Moisture /Miscellaneous	100.0%

What is claimed is:

1. A detergent composition comprising:
   (a) alkali metal percarbonate
   (b) one or more alkyl polysaccharides of formula

$$RO(C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from a saccharose; R is a saturated hydrophobic alkyl group that contains from 8 to 20 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 10.

2. A composition according to claim 1 comprising said alkali metal percarbonate in an amount of at least 9% by weight of total composition.

3. A composition according to claim 1 or claim 2, wherein Z is a moiety derived from glucose.

4. A composition according to any preceding claim, wherein x is from 1.1 to 4, preferably 1.2 to 2.

5. A composition according to any preceding claim, wherein R is a saturated hydrophobic alkyl group that contains from 12 to 18, preferably 12 to 14, carbon atoms.

6. A composition according to any preceding claim, wherein t is 0.

7. A composition according to any preceding claim comprising one or more anionic surfactants wherein the ratio of the total weight of said anionic surfactants to the weight of said one or more alkyl polysaccharides is at least 1.

8. A composition according to claim 7, wherein the ratio of the total weight of said one or more anionic surfactants to the weight of said one or more alkyl polysaccharides is at least 1.5.

9. A composition according to claim 7 or claim 8, wherein said anionic surfactant is an alkyl sulphate.

10. A composition according to any preceding claim, comprising detergent builder in an amount of at least 30%.

11. A composition according to any preceding claim, comprising surfactant in a total amount of from 10 to 25% by weight of total composition.

12. A composition according to any preceding claim additionally comprising additional bleaching agents selected from peroxyacid bleach precursors and organic peroxyacids and mixtures thereof.

13. A composition according to claim 12, wherein the additional bleaching agent is TAED.

14. A composition according to any preceding claim which is a laundry detergent composition.

15. A composition according to any of claims 1 to 13 which is a machine dishwashing composition.

16. A composition according to any of claims 1 to 13 which is a hand dishwashing composition.

17. A process of washing laundry in a domestic washing machine in which an effective amount of a laundry detergent composition is introduced into the wash liquor during the wash, wherein the process is conducted at a temperature of no more than 50°C, and wherein the laundry detergent composition comprises

(a) an alkali metal percarbonate

(b) one or more alkyl polysaccharides of formula

$$RO(C_nH_{2n}O)_tZ_x$$

wherein Z is a moiety derived from a saccharose; R is a saturated hydrophobic alkyl group that contains from 8 to 20 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.1 to 10.

18. A process according to claim 17, wherein the laundry comprises hydrophobic material.

19. A process according to claim 17 or claim 18, wherein the process is conducted at a temperature of between 10 and 35°C.

20. A process according to any of claims 17 to 19, wherein the detergent composition is a composition according to any of claims 2 to 14.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07826

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C11D 3/395, 9/00, 1/12, 1/755
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. : 252/94, 108, 174.17, 174.18, 550, DIG 11, DIG, 13, DIG 14, DIG 15

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A, 0,267,042 (Anderson, et al.) 11 May 1988, pages 1-63	1-3, 17-19
Y,P	US, A, 5,266,690 (McCURRY et al.) 30 November 1993, col. 2, line 45 to col. 15, line 69.	1-3, 17-19

☐ 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 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 disclosure, use, exhibition or other means

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

16 SEPTEMBER 1994

Date of mailing of the international search report

12 OCT 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07826

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

252/94, 108, 174.17, 174.18, 550, DIG 11, DIG, 13, DIG 14, DIG 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07826

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.: 4-16, 20
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.