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(54) Granular detergent-bleaching compositions.

(57) This invention relates to granular detergent-bleaching compositions that provide effective and efficient bleaching of textiles over a wide range of bleach solution temperatures. The bleaching compositions within the invention contain peroxygen bleaches capable of yielding hydrogen peroxide in aqueous solutions and specific bleach activators comprising at least about 10% capable of providing C₁₀ acylperoxyacids, at molar ratios of hydrogen peroxide to bleach activator of about 1.5. In another embodiment the invention relates to preferred mixtures of bleach activators.

GRANULAR DETERGENT-BLEACHING COMPOSITIONS

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TECHNICAL FIELD

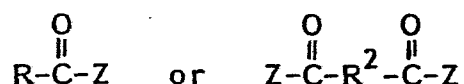
This invention relates to granular detergent-bleaching compositions. More particularly, this invention relates to detergent-bleaching compositions that provide effective and efficient surface bleaching of soils in laundry processes over a wide range of bleach solution temperatures without excessive damage to dyed fabrics. The detergent-bleaching compositions within the invention contain peroxygen bleaches capable of yielding hydrogen peroxide in aqueous solutions and specific bleach activators. This invention also relates to mixtures of activators that are especially useful in such compositions

It has long been known that peroxygen bleaches are effective for stain and/or soil removal from textiles, but that they are also extremely temperature dependent. Such bleaches are essentially only practicable and/or effective in bleaching solutions, i.e., a bleach and water mixture, wherein the solution temperature is above about 60°C. At bleach solution temperatures of about 60°C peroxygen bleaches are only partially effective and, therefore, in order to obtain a desirable level of bleaching performance extremely high levels of peroxygen bleach must be added to the system. This is economically impracticable. As the bleach solution temperature is lowered below 60°C., peroxygen bleaches are rendered ineffective, regardless of the level of peroxygen bleach added to the system. The temperature dependence of peroxygen bleaches is significant because such bleaches are commonly used as a detergent adjuvant in textile wash processes that utilize an automatic household washing machine at wash water temperatures below 60°C. Such wash temperatures are utilized because of textile care and energy considerations. As a consequence of such a wash process, there has been much industrial research to develop substances, generally referred to as bleach activators, that render peroxygen bleaches effective at

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bleach solution temperatures below 60°C. Numerous substances have been disclosed in the art as effective bleach activators.

U.S. Patent 4,283,301, Diehl (August 11, 1981), discloses bleaching compositions comprising a peroxygen bleach and a
5 bleach activator of the general formula:



wherein R is an alkyl chain containing from about 5 to about 13 carbon atoms, R² is an alkyl chain containing from about 4 to
10 about 24 carbon atoms and each Z is a leaving group as defined therein. It is preferred that such bleaches and bleach activators are present in equimolar ratios.

U.S. Patent 4,412,934 discloses compositions containing bleach activators with the formula

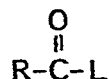


where R contains from 5 to 18 carbon atoms and L is a leaving group, the molar ratio of perborate to activator being greater than about 1.5. Said patents are incorporated herein by
20 reference.

SUMMARY OF THE INVENTION

The present invention comprises a granular detergent-bleaching composition comprising:

- (a) a peroxygen bleaching compound capable of yielding
25 hydrogen peroxide in an aqueous solution;
- (b) from about 0.1% to about 40% of a bleach activator having the general formula:



wherein R is an alkyl group containing 9 carbon atoms in at least about 10% of the activator and the remainder of the R groups contain from about 6 to about 10 carbon atoms, and L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 6 to
35 about 13;

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(c) from about 1% to about 50% of detergent surfactant; and
(d) from 0% to about 70% of detergent builder,
wherein the molar ratio of hydrogen peroxide yielded by (a) to
bleach activator (b) is greater than about 1.

5 DETAILED DESCRIPTION OF THE INVENTION

This invention relates to granular solid detergent-bleaching
compositions containing peroxygen bleaches capable of yielding
hydrogen peroxide in an aqueous solution and specific bleach
activators, hereinafter defined, at specific molar ratios of
10 hydrogen peroxide to bleach activator. Such compositions provide
extremely effective and efficient detergency and surface
bleaching. The compositions are particularly effective when used
to remove dingy soils from textiles. Dingy soils are soils that
build up on textiles after numerous cycles of usage and washing
15 and, thus, result in a white textile having a gray or yellow tint.
These soils tend to be a blend of particulate and greasy materi-
als. The removal of this type of soil is sometimes referred to as
"dingy fabric clean up".

The detergent-bleaching compositions of this invention
20 provide such bleaching over a wide range of bleach solution
temperatures. Such bleaching is obtained in detergent-bleach
solutions wherein the solution temperature is at least about 5°C.
Without the bleach activator such peroxygen bleaches would be
ineffective and/or impracticable at temperatures below about 60°C.

25 In U.S. Patent 4,412,934, Column 14, line 11, et seq. there
is a disclosure that the C₁₀ acyl activator of this invention is less
desirable because much less (58%) of the C₁₀ acyl group converts
to the percarboxylic acid than the C₈ (83%). However, it has
now been discovered that the actual performance of the C₁₀ acyl
30 activator is equal to or better than that of the analagous C₈ and
C₉ acyl bleach activators which are preferred in U.S. 4,412,934.
This level of performance was totally unexpected. This discovery
allows the use of mixtures of fatty acyl activators containing
appreciable amounts of C₁₀ acyl groups. As a result, separation

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and/or purification steps can be less thorough without a loss in performance. In addition, the improvement in odor from using mixtures of activators with even small amounts of C_{10} acyl groups is surprisingly large.

- 5 It is desirable to use at least about 10% C_{10} acyl groups, preferably at least about 20%, and up to 100% is feasible, without loss in performance.

10 The most surprising advantage of using activators containing C_{10} acyl groups is the improvement in safety to dyed fabrics which results. When solid detergent-bleach compositions comprising activated bleach systems of the type described in U.S. Patent 4,412,934 become entrapped in fabrics, there is a potential for damage to bleach sensitive dyes. Bleach activators containing C_{10} acyl groups provide a remarkably safe solid detergent-bleach
15 composition that gives significantly less damage to bleach sensitive dyes, even under stressed conditions than does the corresponding C_8 or C_9 acyl group.

20 The molar ratio of hydrogen peroxide yielded by the peroxygen bleach to bleach activator is at least about 1. For best performance the molar ratio should be greater than about 1.5 and preferably at least about 2.0. Surprisingly, increasing such molar ratio above 1.5 results in not only faster formation of the percarboxylic acid, but, most importantly, more percarboxylic acid being formed. With a molar ratio of such components of
25 about 1 or less there are competing chemical reactions which become a significant factor. For example, the activator may hydrolyze to carboxylic acid before it perhydrolyzes. In addition, the percarboxylic acid that is formed can further react with the unreacted bleach activator to form a diacyl peroxide.
30 Consequently, lower concentrations of percarboxylic acid are ultimately achieved and, therefore, bleaching performance is lowered. Such competing chemical reactions are minimized by the addition of more peroxygen bleach. Accordingly, bleaching performance is enhanced, especially for dingy fabrics.

There is essentially no upper limit to such molar ratio from a bleaching standpoint because the addition of more peroxygen bleach is not detrimental to the system. However, at ratios above about 10 essentially all of the theoretical amount of percarboxylic acid that can be formed is formed. It is not economically practicable or desirable to add more peroxygen bleach. However, if one is bleaching at bleach solution temperatures wherein a bleach activator is not required to activate the peroxygen bleach, i.e., above 60°C., then more peroxygen bleach can be added and it does provide an additional benefit. This is particularly true under European wash conditions that utilize a "boil wash". Also, it is common for European detergent compositions to contain extremely high levels of peroxygen bleach. Based upon this, the upper limit of the molar ratio of hydrogen peroxide yielded by the peroxygen bleach to bleach activator is about 500.

It should be noted that such ratio can generally be expressed as the molar ratio of peroxygen bleach to bleach activator because the vast majority of peroxygen bleaches yield one mole of hydrogen peroxide per mole of peroxygen bleach. One mole of bleach activator is equal to one acyl group which can undergo perhydrolysis to form a peroxyacid.

Optimum bleaching performance is obtained with detergent-bleaching solutions wherein the initial pH of such solution is between about 8.5 and 10.5 and preferably between 9 and 10.3. It is preferred that such pH be greater than 9 to optimize the perhydrolysis reaction and thus surface bleaching performance, and also to help prevent the bleaching solution from having an undesirable odor. When the pH drops, however, the solution odor of C₁₀ acyl activator is better than that of C₈ or C₉ acyl activators when they are used alone. With the preferred mixtures of activators, the solution odor is also much less noticeable. Such pH can be obtained with substances commonly known as buffering agents, which are optional components of the bleaching compositions herein.

The following is a detailed description of the essential and the optional components of the solid detergent-bleaching compositions within the invention. All percentages, parts and ratios

are by weight unless otherwise indicated.

The Peroxygen Bleaching Compound

The peroxygen bleaching compounds useful herein are those capable of yielding hydrogen peroxide in an aqueous solution.

5 These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or
10 more such bleaching compounds can also be used, if desired.

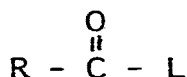
Preferred peroxygen bleaching compounds include sodium perborate, commercially available in the form of mono- and tetrahydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide.

15 Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching solution. It is believed that such rapid dissolution
20 results in the formation of higher levels of peroxycarboxylic acid and, thus, enhanced surface bleaching performance.

The level of peroxygen bleach within compositions of the invention is from about .1% to about 60% and preferably from about 1% to about 20%.

25 The Bleach Activator

The bleach activators within the invention have the general formula:



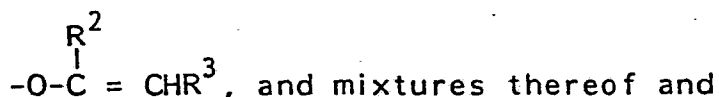
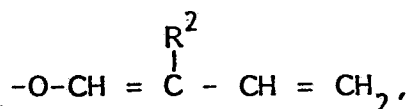
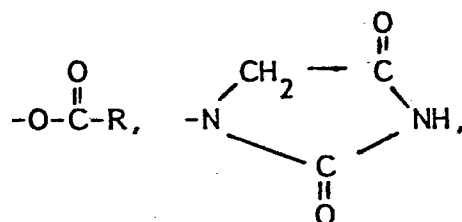
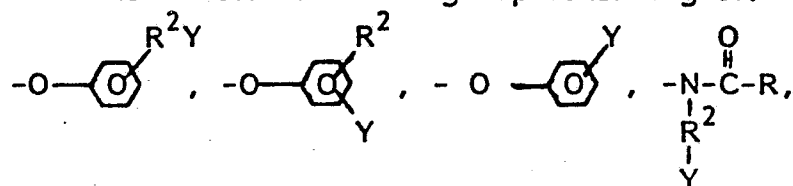
30 wherein R is an alkyl group containing 9 carbon atoms in at least about 10% of the activator, the remainder of the alkyl groups containing from about 7 to about 10 carbon atoms, and L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 6 to about 13.

35 L can be essentially any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator

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by the perhydroxide anion. This, the perhydrolysis reaction, results in the formation of the peroxy-carboxylic acid. Generally, for a group to be a suitable leaving group it must exert an electron attracting effect. This facilitates the nucleophilic attack
 5 by the perhydroxide anion. Leaving groups that exhibit such behavior are those in which their conjugate acid has a pK_a in the range of from about 6 to about 13, preferably from about 7 to about 11 and most preferably from about 8 to about 11.

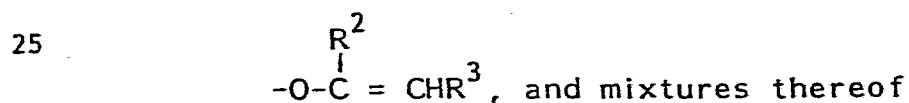
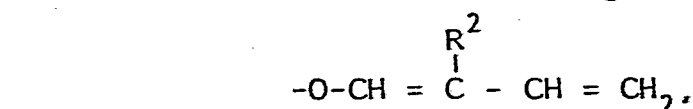
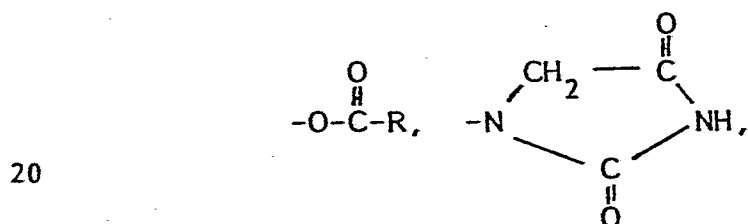
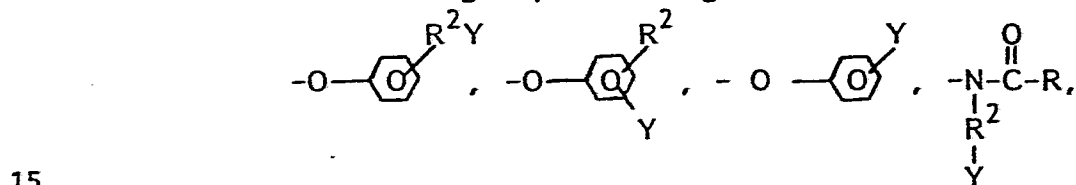
Preferred bleach activators are those of the above general
 10 formula wherein L is selected from the group consisting of:



wherein R is as defined in the general formula, R^2 is an alkyl chain containing from about 1 to about 8 carbon atoms, R^3 is H or R^2 , and Y is H or a solubilizing group. The preferred
 30 solubilizing groups are $-\text{SO}_3^- \text{M}^+$, $-\text{COO}^- \text{M}^+$, $-\text{SO}_4^- \text{M}^+$, $(-\text{N}^+ \text{R}_3^4) \text{X}^-$ and $-\text{NR}_2^4 \rightarrow \text{O}$ and most preferably $-\text{SO}_3^- \text{M}^+$ and $-\text{COO}^- \text{M}^+$ wherein R^4 is an alkyl chain containing from about 1 to about 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the
 35 bleach activator. Preferably, M is an alkali metal, ammonium or

substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion. The bleach activators preferably have a leaving group that contains a solubilizing group in order to assist in their dissolution.

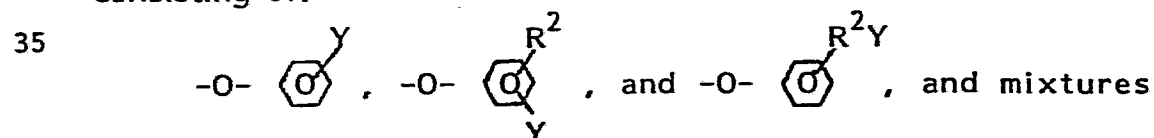
Preferred bleach activators are those of the above general formula wherein R is a mixture of linear alkyl chains. The preferred bleach activators contain R groups which are linear alkyl chains of which from about 10% to about 90% contain 9 carbon atoms, more preferably from about 20% to about 80%, and L is selected from the group consisting of:



wherein R, R², R³ and Y are as defined above.

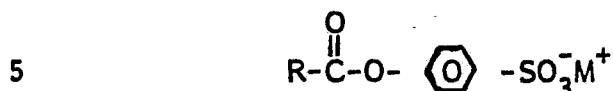
Preferably less than about 70%, most preferably less than about 50% of the activator contains any single acyl group, for odor reasons.

Particularly preferred bleach activators are those of the above preferred formulas wherein L is selected from the group consisting of:



thereof wherein R^2 is as defined above and Y is $-\text{SO}_3^- \text{M}^+$ or $-\text{COO}^- \text{M}^+$ wherein M is as defined above.

The most preferred bleach activators have the formula:



wherein R is a mixture of linear alkyl chain containing from about 7 to about 10 carbon atoms of which at least about 10% contain 9 carbon atoms, and M is sodium or potassium.

The preferred mixture of activators comprises at least two
 10 different acyl chain lengths containing from about 8 to about 10 carbon atoms ($R = C_7$ to C_9), there being no one acyl chain length in more than about 70% of the activator and no less than 10%, preferably no less than 20% of the activator containing a C_{10} acyl chain ($R = C_9$). Particularly preferred are 60/40 mixtures of
 15 C_8 and C_{10} acyl chains alone and in combination with a C_9 acyl chain. Mixtures of C_9 and C_{10} acyl groups are even more preferred. These mixtures preferably have the leaving groups L which are indicated as being preferred hereinbefore, and have linear alkyl chain R groups. Such mixtures have surprisingly
 20 better odor characteristics.

The level of bleach activator within the compositions of the invention is from about .1% to about 40%, preferably from about .5% to about 20%, most preferably from about 1% to about 5%.

The Detergent Surfactant

25 The solid detergent-bleaching compositions of the invention contain detergent surfactant.

The detergent surfactant can be any one or more surface active agents selected from anionic, nonionic, zwitterionic, amphoteric and cationic classes and compatible mixtures thereof.
 30 Detergent surfactants useful herein are listed in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin et al, issued December 30, 1975, both incorporated herein by reference. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell,
 35 issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980, both incorporated herein by

reference. The following are representative examples of detergent surfactants useful in the present compositions.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This
5 includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils, or by the neutralization of free
10 fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium
15 salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the
20 sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in
25 straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13} LAS.

30 Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from
35 about 1 to about 10 units of ethylene oxide per molecule and

wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10, preferably from about 1 to about 3, units of ethylene oxide per molecule and wherein the
5 alkyl group contains from about 10 to about 20, preferably from about 14 to about 16, carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from
10 about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin and paraffin sulfonates containing from about 12 to 20 carbon
15 atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Water-soluble nonionic surfactants are also useful in the compositions of the invention. Such nonionic materials include
20 compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-
25 soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of
30 alkyl phenols having an alkyl group containing from about 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from about 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8
35 to 22 carbon atoms, in either straight chain or branched config-

uration, with from 3 to 12 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 8 moles of ethylene oxide per mole of alcohol.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic, quaternary, ammonium, phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

The level of detergent surfactant that is employed is from about 1% to about 50%, preferably from about 5% to about 30% and most preferably from about 10% to about 25% by weight of the total composition.

The Detergent Builder

In addition to detergent surfactant, detergency builder can be employed in the granular bleaching compositions. Water-soluble inorganic or organic electrolytes are suitable builders. The builder can also be water-insoluble calcium ion

exchange materials. Nonlimiting examples of suitable water-soluble, inorganic detergent builders include: alkali metal carbonates, borates, phosphates, bicarbonates and silicates. Specific examples of such salts include sodium and potassium tetraborates, bicarbonates, carbonates, orthophosphates, pyrophosphates, tripolyphosphates and metaphosphates.

Examples of suitable organic alkaline detergency builders include: (1) water-soluble amino carboxylates and aminopolyacetates, for example, nitrilotriacetates, glycinate, ethylenediamine-tetraacetates, N-(2-hydroxyethyl)nitrilodiacetates and diethylenetriaminepentaacetates; (2) water-soluble salts of phytic acid, for example, sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium, and lithium salts of ethane-1-hydroxy-1, 1-diphosphonic acid; sodium, potassium, and lithium salts of ethylenediphosphonic acid; and the like; (4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethyloxysuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, mellitic acid and pyromellitic acid; and (5) water-soluble polyacetals as disclosed in U.S. Patents 4,144,266 and 4,246,495 incorporated herein by reference.

Another type of detergency builder material useful in the present compositions comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, particularly those described in Belgian Patent 814,874, issued November 12, 1974, incorporated herein by reference. This patent discloses and claims detergent compositions containing sodium aluminosilicates having the formula:



wherein z and y are integers equal to at least 6, the molar ratio of z to y is in the range of from 1.0:1 to about 0.5:1, and X is an integer from about 15 to about 264, said aluminosilicates having a calcium ion exchange capacity of at least 200 milligrams equivalent/gram and a calcium ion exchange rate of at least about 2 grains/gallon/minute/gram. A preferred material is Zeolite A which is:



The level of detergency builder of the bleaching compositions is from 0% to about 70%, preferably from about 10% to about 60%, and most preferably from about 20% to about 60%.

Optional Ingredients

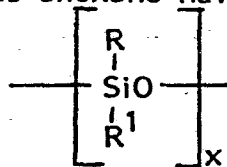
The bleaching compositions of this invention can contain all of the usual components of detergent compositions including the ingredients set forth in U.S. Patent 3,936,537, Baskerville et al, incorporated herein by reference. Such components include color speckles, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil-release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, perfumes, etc.

Buffering agents can be utilized to maintain the desired alkaline pH of the detergent-bleaching solutions. Buffering agents include, but are not limited to many of the detergency builder compounds disclosed hereinbefore. Buffering agents suitable for use herein are those well known in the detergency art.

Preferred optional ingredients include suds modifiers particularly those of suds suppressing types, exemplified by silicones, and silica-silicone mixtures.

U.S. Patents 3,933,672, issued January 20, 1976 to Bartolotta et al, and 4,136,045, issued January 23, 1979 to Gault et al, incorporated herein by reference, disclose silicone suds controlling agents. The silicone material can be represented by alkylated polysiloxane materials such as silica aerogels and xero-

gels and hydrophobic silicas of various types. The silicone material can be described as siloxane having the formula:



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wherein x is from about 20 to about 2,000 and R and R¹ are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl and phenyl. The polydimethylsiloxanes (R and R¹ are methyl) having a molecular weight within the range of from about 200 to about 2,000,000, and higher, are all useful as suds controlling agents. Additional suitable silicone materials wherein the side chain groups R and R¹ are alkyl, aryl, or mixed alkyl or aryl hydrocarbyl groups exhibit useful suds controlling properties. Examples of the like ingredients include diethyl-, dipropyl-, dibutyl-, methyl-, ethyl-, phenylmethylpolysiloxanes and the like. Additional useful silicone suds controlling agents can be represented by a mixture of an alkylated siloxane, as 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 trimethylsilanated) silica having a particle size in the range from about 10 millimicrons to 20 millimicrons and a specific surface area above about 50 m²/gm. 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 19:1 to about 1:2. The silicone suds suppressing agent is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier.

Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in U.S. Patent 4,073,118, Gault et al, issued February 21, 1978, incorporated herein by reference. An example of such a compound is DB-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

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Suds modifiers as described above are used at levels of up to approximately 2%, preferably from about 0.1 to about 1½% by weight of detergent surfactant.

Microcrystalline waxes having a melting point in the range from 35°C-115°C and a saponification value of less than 100 represent additional examples of preferred suds control components for use in the subject compositions, and are described in detail in U.S. Patent 4,056,481, Tate, issued November 1, 1977, incorporated herein by reference. The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes have a melting point from about 65°C to 100°C, a molecular weight in the range from 400-1,000; and a penetration value of at least 6, measured at 77°F by ASTM-D1321. Suitable examples of the above waxes include: microcrystalline and oxidized microcrystalline petroleum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax; candle-lilla; and carnauba wax.

Alkyl phosphate esters represent an additional preferred suds control agent for use herein. These preferred phosphate esters are predominantly monostearyl phosphate which, in addition thereto, can contain di- and tristearyl phosphates and monooleyl phosphate, which can contain di- and trioylel phosphate.

Other suds control agents useful in the practice of the invention are the soap or the soap and nonionic mixtures as disclosed in U.S. Patents 2,954,347 and 2,954,348, incorporated herein by reference.

All percentages, parts and ratios herein are by weight unless otherwise indicated.

The following examples are given to illustrate the parameters of and compositions within the invention.

EXAMPLE I

The following granular detergent composition was prepared:

		<u>g</u>
	Sodium C ₁₄₋₁₅ alkyl sulfate	7.5
	Sodium C ₁₃ linear alkylbenzene sulfonate	7.5
	C ₁₂₋₁₃ alkyl polyethoxylate _{6.5T} *	1.0
5	C ₁₂ alkyltrimethyl ammonium chloride	1.0
	Sodium tripolyphosphate	32.0
	Sodium carbonate	12.0
	Sodium sulfate	10.1
	Sodium silicate (1.6r)	5.0
10	Miscellaneous (e.g., perfume, optical brightener, protease enzyme, suds suppressor, chelating agent, polyethylene glycol, etc.)	Balance

*Stripped of lower ethoxylated fractions and fatty alcohol.

15 Fabrics are prepared by splitting dirty, dingy T-shirts, pillowcases, and dish towels into swatches. Terry cloth towels are preconditioned with artificial body soils so as to simulate household laundry. Other fabric swatches were stained with six different bleachable stains.

20 Each laundry load consists of five terry cloth towels, nine dingy swatches (3 each from T-shirts, pillow cases, and towels), and six different stained swatches.

 The laundry loads are washed in the mini-wash system with a quantity of the above detergent composition that corresponds to
 25 1250 ppm in the wash water (which is typical of conventional automatic wash processes) and, as required, a bleach system containing sodium perborate monohydrate and a sodium fatty acyloxybenzene sulfonate. The mini-wash system with such a load simulates a conventional automatic wash process. The wash water
 30 temperature was 37°C. and the rinse water temperature was 22°C. and both contained 2 gallons of water with 5 grains/gallon hardness.

 The following tests were carried out in the mini-wash systems. In one series of tests the detergent composition was one
 35 treatment and three additional treatments contained the detergent

composition and 1:1 mixtures of sodium perborate monohydrate and sodium C₈ fatty acyloxybenzene sulfonate (bleach activator) at total concentrations of 90, 180, and 270 ppm respectively for the perborate/bleach activator mixture. In a second series of tests the detergent composition was one treatment and in three additional treatments the detergent composition and mixtures of sodium perborate and sodium C₁₀ acyloxybenzene sulfonate were used, the level of sodium perborate monohydrate being the same as in the first series of tests and the sodium C₁₀ acyloxybenzene sulfonate being substituted for the sodium C₈ acyloxybenzene sulfonate of the first series on an equal molar basis. There were four replicates of each process. For each of these bleaching systems the molar ratio of hydrogen peroxide yielded by sodium perborate to bleach activator was 3.

Each of the dingy swatches was then comparison graded with its original other half to determine relative stain removal. A grading scale of -4 to 4 was used, with -4 indicating much less stain removal, 0 indicating no difference and 4 indicating much more stain removal. The average of the grades for each fabric of each mini-wash system was calculated.

The swatches that are felt to most accurately reflect bleach performance are dingy T-shirts, pillow cases (PC), and dish towels (DT). These swatches were graded against the product with no bleach present. These paired comparisons were as follows:

		<u>Bleach activator/perborate</u>	
		<u>45/45 ppm</u>	<u>49/45 ppm</u>
		<u>C₈</u>	<u>C₁₀</u>
30	T-shirts	2.16	1.83
	PC	1.25	1.83
	DT	<u>1.42</u>	<u>1.50</u>
		1.61	1.72 difference =+0.11

Bleach activator/perborate

		<u>90/90 ppm</u>	<u>98/90 ppm</u>
		<u>C₈</u>	<u>C₁₀</u>
5	T-shirts	1.92	2.17
	PC	1.42	2.00
	DT	<u>1.75</u>	<u>2.33</u>
		1.70	2.17 difference =+0.47

Bleach activator/perborate

		<u>135/135 ppm</u>	<u>147/135 ppm</u>
		<u>C₈</u>	<u>C₁₀</u>
10	T-shirts	2.17	2.25
	PC	1.33	2.00
15	DT	<u>1.92</u>	<u>2.00</u>
		1.81	2.08 difference =+0.27

Based on prior experience with such systems it is clear that the decanoyloxybenzene sulfonate is better, or at least equal to the octanoyloxybenzene sulfonate.

20 EXAMPLE II

The granular detergent compositions herein had the general formula:

		<u>Components</u>	<u>%</u>
		Sodium C ₁₄₋₁₅ alkyl sulfate	7.5
25		Sodium C ₁₃ linear alkylbenzene sulfonate	7.5
		C ₁₂₋₁₃ alkyl polyethoxylate _{6.5T*}	1.0
		C ₁₂ alkyltrimethyl ammonium chloride	1.0
		Sodium tripolyphosphate	32.0
		Sodium carbonate	12.0
30		Sodium sulfate	10.1
		Sodium perborate monohydrate	3.0
		Sodium fatty acyloxybenzene sulfonate	3.0
		Sodium silicate (1.6r)	5.0
35		Miscellaneous (e.g., perfume, optical brightener, chelating agent, polyethylene glycol, etc.)	Balance

Four colored fabrics were selected to represent those classes of dyes that are susceptible to color fading due to oxygen bleaching. The fabrics were cut into 5x5 inch swatches. 10% of the normal product usage (9.65 grams) was placed into the middle of the swatch which was then folded into a pocket. The pocket was formed by folding 1/3 of the swatch over the product, folding the remaining third over the fabric and stapling closed the ends and long edge of the pocket. Enclosing the product as described allows the product to slowly dissolve during the fill and wash cycles.

The different fabric swatches for each treatment were placed at the bottom of a Kenmore top loading automatic washer and then covered with 5.5 pounds of clean ballast items. City and soft water (about 6 grains of calcium and magnesium hardness total) were used which took about 5 minutes to fill before the 12 minute regular wash. The water temperature was 95°F.

Each treatment consisted of a granular detergent as described above. The acyl groups for the sodium fatty acyloxybenzene sulfonate were 100% heptanoyl (C_7), octanoyl (C_8), nonanoyl (C_9) or decanoyl (C_{10}). Each experiment was replicated twice.

The colored swatches were round robin graded against each other using a grading scale of -4 to 4 with -4 indicating much more color fading, 0 indicating no difference, and 4 indicating much less color fading.

The results were as follows:

		<u>Score - Normalized to C₁₀</u>				
Acyl Chain length		7	8	9	10	
<u>Color/Dye Type</u>						<u>LSD₉₅</u>
30	Red Naphthol	-3.3	-2.4	-1.6	0.0	1.2
	Green Direct	-0.1	0.1	0.0	0.0	0.5
	Brown Sulfur	-2.2	-0.9	-1.1	0.0	1.4
	Green Sulfur	<u>-1.8</u>	<u>-1.6</u>	<u>-1.9</u>	<u>0.0</u>	<u>1.2</u>
	Overall Average	-1.8	-1.0	-1.1	0.0	1.1

The decanoyl (C_{10}) variation surprisingly provides less color fading than the lower chain lengths.

EXAMPLE III

The following granular detergent compositions were prepared:

Components	%
Sodium C_{14-15} alkyl sulfate	7.5
Sodium C_{13} linear alkylbenzene sulfonate	7.5
C_{12-13} alkyl polyethoxylate _{6.5T*}	1.0
C_{12} alkyltrimethyl ammonium chloride	1.0
Sodium tripolyphosphate	32.0
Sodium carbonate	12.0
Sodium sulfate	10.1
Sodium perborate monohydrate	As Indicated
Sodium fatty acyloxybenzene sulfonate	As Indicated
Sodium silicate (1.6r)	5.0
Miscellaneous (e.g., perfume, optical brightener, chelating agent, polyethylene glycol, enzymes, etc.)	Balance

20

Fabrics, including soiled swatches, dingy fabrics, and clean ballast terry cloths, were washed in a mini-washer using 125°F city water and 1500 ppm of the detergent product. The water was added first, the fabrics next and the product last. The wash cycle took 12 minutes. The 125°F is a stress condition since lower temperatures are more common and the higher temperature drives off more of the undesirable odoriferous materials.

In Treatment A, the product contained 9% perborate and 3% C_8 acyloxybenzene sulfonate; in Treatment B, the product contained 3.5% perborate and 3% C_9 acyloxybenzene sulfonate; and in treatment C, the product contained 3.5% perborate and 3.0% C_{10} acyloxybenzene sulfonate. The solutions gave the following odor results.

A's solution had a strong odor which was characterized as a sour, acidic, bleach off-odor.

B's solution had a strong odor which was characterized as a rancid, fatty, bleach off-odor.

C's solution had a slight odor characterized as an oily, burnt off-odor.

- 5 The product containing C₁₀ acyloxybenzene sulfonate was clearly and surprisingly superior from an odor standpoint as compared to similar compositions containing the lower adjacent homologs.

CLAIMS

1. A granular detergent-bleaching composition comprising:
 - (a) a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous solution;
 - (b) from about 0.1% to about 40% of a bleach activator

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wherein R is an alkyl group containing 9 carbon atoms in at least about 10% of the activator and the remainder of the R groups contain from about 7 to about 10 carbon atoms, and L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 6 to about 13;

15

- (c) from about 1% to about 50% of a detergent surfactant; and

- (d) from 0% to about 70% of a detergent builder,

wherein the molar ratio of hydrogen peroxide yielded by (a) to bleach activator (b) is greater than about 1.

2. The composition of Claim 1 wherein the molar ratio of hydrogen peroxide yielded by (a) to bleach activator (b) is at least about 1.5.

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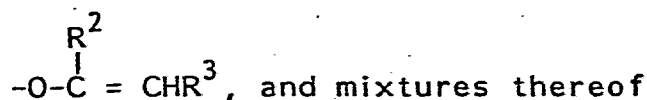
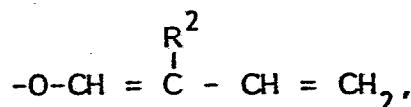
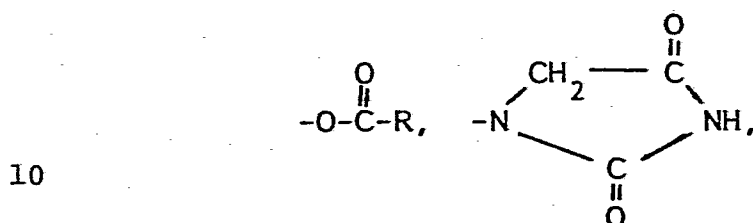
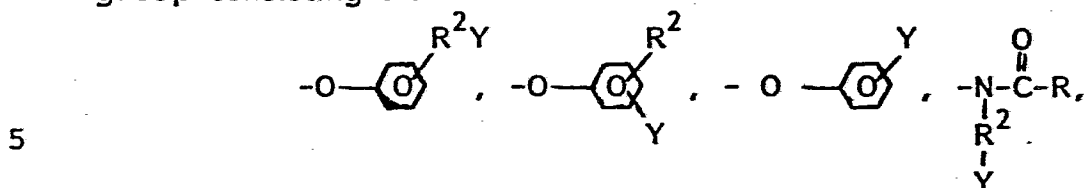
3. The composition of Claim 2 wherein the peroxygen bleaching compound is selected from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide and mixtures thereof.

4. The composition of Claim 3 wherein the peroxygen bleaching compound is sodium perborate monohydrate.

5. The composition of Claim 2 wherein L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 7 to about 11.

6. The composition of Claim 5 wherein L is a leaving group, the conjugate acid of which has a pK_a in the range of from about 8 to about 11.

7. The composition of Claim 2 wherein L is selected from the group consisting of:



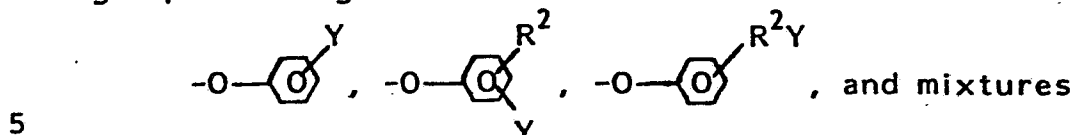
15 wherein R is as defined in Claim 1, R^2 is an alkyl chain containing from about 1 to about 8 carbon atoms, R^3 is H or R^2 , and Y is H or a solubilizing group.

8. The composition of Claim 7 wherein Y is selected from the group consisting of: $-\text{SO}_3^-\text{M}^+$, $-\text{COO}^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $(-\text{N}^+\text{R}_3^4)\text{X}^-$ and $-\text{NR}_2^4\text{O}$ and mixtures thereof wherein R^4 is an alkyl chain containing from about 1 to about 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator.

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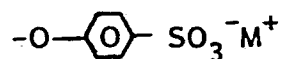
9. The composition of Claim 8 wherein Y is selected from the group consisting of $-\text{SO}_3^- \text{M}^+$, $-\text{COO}^- \text{M}^+$ and mixtures thereof wherein M is selected from the group consisting of sodium, potassium and mixtures thereof.

10. The composition of Claim 7 wherein L is selected from the group consisting of:



thereof wherein R^2 is an alkyl chain containing from about 1 to about 8 carbon atoms, Y is $-\text{SO}_3^- \text{M}^+$ or $-\text{COO}^- \text{M}^+$ wherein M is sodium or potassium.

11. The composition of Claim 10 wherein L has the general formula:



wherein M is sodium or potassium.

12. The composition of Claim 1 containing

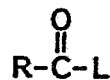
- 5 (a) from about 1% to about 60% peroxygen bleaching compound;
- (b) from about .5% to about 20% bleach activator and at least about 20% of the R groups contain 9 carbon atoms;
- (c) from about 5% to about 30% detergent surfactant;
- (d) from about 10% to about 60% detergent builder; and
- a molar ratio of hydrogen peroxide yielded by (a) to bleach activator (b) of greater than about 2.

13. The composition of Claim 12 containing

- 5 (a) from about 1% to about 20% peroxygen bleaching compound;
- (b) from about 1% to about 5% bleach activator and at least about 20% of the R groups contain 9 carbon atoms;
- (c) from about 10% to about 25% detergent surfactant;
- (d) from about 20% to about 60% detergent builder; and

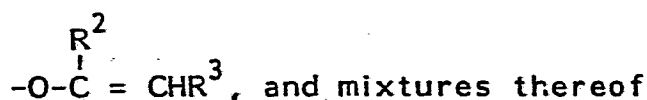
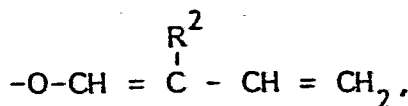
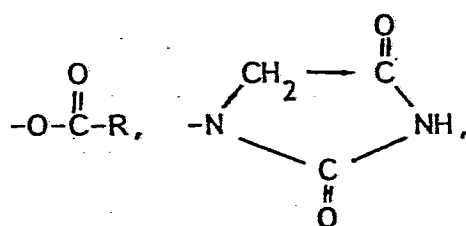
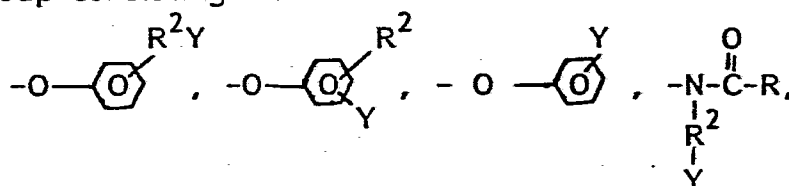
a molar ratio of hydrogen peroxide yielded by (a) to bleach activator (b) of from about 2 to about 10.

14. A bleach activator composition consisting essentially of a mixture of bleach activators having the general formula



5 wherein R is an alkyl group containing from about 8 to about 10 carbon atoms, wherein there are at least two different R groups, none of which is in more than about 70% of said activator, and at least about 10% of said activator containing an R group containing 9 carbon atoms; and wherein L is a leaving group, the conjugate
10 acid of which has a pK_a in the range of from about 6 to about 13.

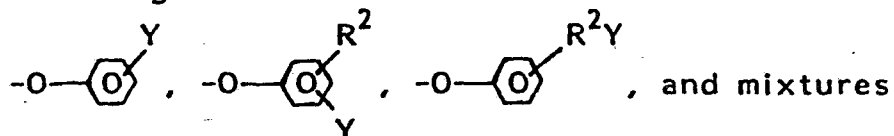
15. The composition of Claim 14 wherein L is selected from the group consisting of:



wherein R is a linear alkyl and in at least about 20% of said bleach activators contains 9 carbon atoms, R^2 is an alkyl chain

containing from about 1 to about 8 carbon atoms, R^3 is H or R^2 , and Y is H or a solubilizing group.

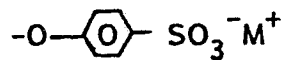
16. The composition of Claim 13 wherein L is selected from the group consisting of:



thereof wherein R^2 is an alkyl chain containing from about 1 to about 8 carbon atoms, Y is $-\text{SO}_3^-\text{M}^+$ or $-\text{COO}^-\text{M}^+$ wherein M is sodium or potassium.

17. The composition of Claim 15 wherein R is a mixture of about 60% C_7 and about 40% C_9 alkyl chains.

18. The composition of Claim 15 wherein L has the general formula:



wherein M is sodium or potassium.



European Patent
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EUROPEAN SEARCH REPORT

0163331
Application number

EP 85 20 0625

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁴)
X	EP-A-0 098 021 (PROCTER & GAMBLE CO.) * page 29, example 6; claims 1-11 *	1-16, 18	C 11 D 3/39
A,P	--- EP-A-0 118 304 (PROCTER & GAMBLE CO.) * page 22, example 1; claims 1,4-7 * -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. ⁴)
			C 11 D 3/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 25-07-1985	Examiner SCHULTZE D
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	