INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4:
C11D 3/386, 3/12

(11) International Publication Number: WO 89/04862
(43) International Publication Date: 1 June 1989 (01.06.89)

(21) International Application Number: PCT/DK88/00189
(22) International Filing Date: 18 November 1988 (18.11.88)
(31) Priority Application Number: 8727081
(32) Priority Date: 19 November 1987 (19.11.87)
(33) Priority Country: GB


(72) Inventors; and

(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DETERGENT COMPOSITIONS CONTAINING CELLULASE GRANULES

(57) Abstract
Detergent compositions for the cleaning and softening of fabrics are claimed, in which cellulase granulates containing a water-insoluble calcium salt, preferably calcium carbonate, are incorporated. Softness and fabric-appearance benefits are excellent. The cellulase granulates per-se are also claimed.
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DETERGENT COMPOSITIONS

CONTAINING CELLULASE GRANULATES

Technical field

The present invention is related to granular detergent compositions which are useful for cleaning and softening of fabrics, and for giving other fabric-care benefits such as appearance improvements and rejuvenation.

The compositions herein contain a fabric-softening clay material, and a cellulase enzyme, which is in the form of granulates containing calcium carbonate.
Background of the Invention

It has been the objective of many detergent manufacturers to formulate laundry detergent compositions which provide the good cleaning performance expected of them, and which also exhibit fabric-care properties, inclusive of softness.

Representative of such detergent compositions are the ones which have been disclosed in British patent 1,514,275 - 1,400,898, or EPA 0 026 528.

Cellulase enzymes have already been used in detergent compositions for their cleaning abilities, as disclosed in British Patent Application GB-A 2,095,275, GB-2,094,826, or Japanese patent 57108-199.

Cellulases have also been found to give softness benefits to fabrics, as in U.S. 4,435,307;

EP-A 0 120 528 teaches alkaline softening detergent compositions comprising a synergistic mixture of a water-insoluble C_{10-26} tertiary amine and cellulase.

EP-A 0 177 165 discloses alkaline softening detergent compositions containing a mixture of smectite clay and cellulase.

EP-A 0 220 016 discloses the fabric color-clarification effect derivable from the use of cellulase in a detergent context.
When such detergent and/or softening compositions are in granular forms, the cellulase enzymes are usually incorporated in the composition in the form of granulates, also identified as marumes, or prills, which are supplied by the enzyme manufacturer.

U.S. 4,435,307, which relates to a hardness reducing agent for detergent compositions, discloses the use of cellulase granulates, and mentions certain ingredients which need to be incorporated to the granulates during their making, for e.g. non-dusting and color purposes.

It has been discovered, however, that certain of these ingredients are detrimental to the softness/fabric care properties of the composition, when cellulase granulates containing these ingredients are incorporated into a detergent composition.

When looking for a replacement to these undesirable ingredients, it has now been discovered that water-insoluble salts of calcium, surprisingly substantially enhance the softness/fabric care performance of the detergent compositions containing the enzyme granulates.

It is therefore the object of the present invention to provide detergent compositions which possess excellent softness/fabric care properties, due to the use of cellulase granulates containing a water-insoluble salt of calcium.

**Summary of the Invention**

The present invention relates to granular detergent compositions containing a fabric-softening clay material, and cellulose granulates containing from 1% to 50%, by weight, preferably 5% to 15% of the granulates, of calcium carbonate.
Calcium carbonate is preferably coated onto the cellulase granulates.

The invention also relates to the above-described cellulase granulates per-se.

Detailed Description of the Invention

The compositions herein are capable of cleaning and softening the treated fabrics, as well as giving benefits in terms of fabric appearance improvements and rejuvenation.

This is achieved by the presence, in the granular compositions herein, of surface active agents, of fabric-softening clay materials, and of cellulase granulates containing calcium carbonate.

In the following, these compulsory, as well as optional ingredients are described in detail:

The Cellulase

The cellulase usable in the present invention may be any bacterial or fungal cellulase having a pH optimum of between 5 and 9.5.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly by the Humicola strain DSM 1800, and cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricula Solander).

Activity determination for the cellulase herein is based on the hydrolysis of carboxymethyl cellulose. Generated low molecular reducing carbohydrates are colorimetrically determined by the ferro cyanide reaction as described by W.S. Hoffman "J. Biol. Chem." 120,51 (1973). Key conditions of incubation are pH = 7.0, temperature of 40° C and incubation time of 20 minutes.

One CMCas e unit is defined as the amount of enzyme which forms per minute an amount of reducing carbohydrate equivalent to 10^{-6} mole of glucose, in the above-described conditions.

A useful range of cellulase activity in the present context is from 5 to 1360, preferably from 60 to 140 CMCase activity units/gram of detergent composition.

The Cellulase Granulates

Cellulase enzymes for use in granular detergent compositions are typically supplied in the form of granulates, e.g. marumes or prills.

Such granulates contain a majority of crude cellulase enzyme, together with additional ingredients, such as polyethylene glycol, at typical levels of from 5 % to 7 %,
and cellulose at typical levels of about 10%. The polyethylene glycol for use herein can have a molecular weight in the range from 500 to 8000.

The amount of cellulase in the granules is determined by the total cellulase activity of the composition, which has to be in the limits set up hereinabove.

It has been discovered that certain materials which have been used by enzyme manufacturers as dustness-preventing and whitening agents, which are Titanium dioxide and Magnesium silicate, interact negatively with the softness performance of the compositions herein.

The compositions of the invention should, therefore, preferably be free of Titanium dioxide and Magnesium silicate.

It has now been found that calcium carbonate possesses the dustness-preventing function when added to the cellulase granulates, and also gives unexpected softness/fabric care benefits as shown hereinafter.

The calcium carbonate should be present in the cellulase granulates, at levels of from 1% to 10%, preferably 5% to 15% by weight, of the granulates.

Calcium carbonates of a particle size range from 1 to 10 microns have been found to be particularly suitable for the purpose of the present invention.
The calcium carbonate used herein may be used as is or in coated form, typically coated with stearic acid. In a preferred execution of the present invention, calcium carbonate, either as is or already coated with e.g. stearic acid, is coated onto the cellulase granulates.

Cellulase granulates can be prepared in a number of different ways, for example by means of a "Marumerizer" as described in British Pat.Nos. 1,362,365 and 1,361,387 or by means of a granulating machine, as described in Aufbereitungs-Technik No. 3/1970, pp. 147-153 and No. 5/1970, pp. 262-278, or can be prilled granulates as described in Belgian Patent Specification No. 760.135. In all cases, the granulates must have low dusting properties.

The calcium carbonate herein is either mixed with the other ingredients during the making of the granulates, or mixed with cellulase before granulation, or, preferably, coated onto the granulates which have been prepared as described hereinabove, by conventional coating methods.

The cellulase granulates according to the present invention are present at levels of from 1% to 50% by weight of the detergent composition herein, preferably 1.5% to 10% by weight.

The surface-active agent

The surface active agent useful herein may be selected from anionic, nonionic, zwitterionic surfactants and is present at levels of from 1% to 50% by weight of the composition, preferably from 10% to 30%.
Suitable anionic surfactants are water-soluble salts of alkyl benzene sulphonates, alkyl sulphates, alkyl polyethoxy ether sulphates, paraffin sulphonates, alpha-olefin sulphonates, alpha-sulphocarboxylates and their esters, alkyl glyceryl ether sulphonates, fatty acid monoglyceride sulphonates and sulphonates, alkyl phenol polyethoxy ether sulphonates, 2-acyloxyalkane-1-sulphonates, and beta-alkyloxy alkane sulphonates.

Especially preferred alkyl benzene sulphonates have 9 to 15 carbon atoms in a linear or branched alkyl chain, especially from 11 to 13 carbon atoms. Suitable alkyl sulphates have from 10 to 22 carbon atoms in the alkyl chain, more especially from 12 to 18 carbon atoms. Suitable alkyl polyethoxy ether sulphates have from 10 to 18 carbon atoms in the alkyl chain and have an average of from 1 to 12 –CH₂CH₂O– groups per molecule, especially from 10 to 16 carbon atoms in the alkyl chain and an average of from 1 to 6 –CH₂CH₂O– groups per molecule.

Suitable paraffin sulphonates are essentially linear and contain from 8 to 24 carbon atoms, more especially from 14 to 18 carbon atoms. Suitable alpha-olefin sulphonates have from 10 to 24 carbon atoms, more especially from 14 to 16 carbon atoms; alpha-olefin sulphonates can be made by reaction with sulphur trioxide, followed by neutralization under conditions such that any sulphates present are hydrolyzed to the corresponding hydroxy alkane sulphonates. Suitable alpha-sulphocarboxylates contain from 6 to 20 carbon atoms; included herein are not only the salts of alpha-sulphonated fatty acids but also their esters made from alcohols containing 1 to 14 carbon atoms.
Suitable alkyl glyceryl ether sulphates are ethers of alcohols having from 10 to 18 carbon atoms, more especially those derived from coconut oil and tallow. Suitable alkyl phenol polyethoxy ether sulphates have from 8 to 12 carbon atoms in the alkyl chain and an average of from 1 to 6 \(-\text{CH}_2\text{CH}_2\text{O}\)-groups per molecule. Suitable 2-acyloxyalkane-1-sulphonates contain from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety. Suitable beta-alkyloxy alkane sulphonates contain from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

The alkyl chains of the foregoing anionic surfactants can be derived from natural sources such as coconut oil to tallow, or can be made synthetically as for example by using the Ziegler or Oxo processes. Water-solubility can be achieved by using alkali metal, ammonium, or alkanol-ammonium cations; sodium is preferred. Mixtures of anionic surfactants are contemplated by this invention; a satisfactory mixture contains alkyl benzene sulphonate having 11-13 carbon atoms in the alkyl group and alkyl sulphate having 12 to 18 carbon atoms in the alkyl group.

Suitable nonionic surfactants to be incorporated in the compositions herein, are water-soluble ethoxylated materials of HLB 11.5-17.0 and include (but are not limited to) \(\text{C}_{10}-\text{C}_{20}\) primary and secondary alcohol ethoxylates and \(\text{C}_6-\text{C}_{10}\) alkylphenol ethoxylates. \(\text{C}_{14}-\text{C}_{18}\) linear primary alcohols condensed with from seven to thirty moles of ethylene oxide per mole of alcohol are preferred, examples being \(\text{C}_{14}-\text{C}_{15}\) (EO)\(_7\), \(\text{C}_{16}-\text{C}_{18}\) (EO)\(_{25}\) and especially \(\text{C}_{16}-\text{C}_{18}\) (EO)\(_{11}\).

Cationic co-surfactants which can be used herein, include water-soluble quaternary ammonium compounds of the
form $R_4R_5R_6N^+X^-$, wherein $R_4$ is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and $R_5$, $R_6$ and $R_7$ are each $C_1$ to $C_7$ alkyl preferably methyl; $X^-$ is an anion, e.g. chloride. Examples of such trimethyl ammonium compounds include $C_{12}-C_{14}$ alkyl trimethyl ammonium chloride and cocoalkyl trimethyl ammonium methosulfate.

The compositions of the invention are essentially free of water-insoluble long-chain alkyl amine softening agents, and derivatives thereof, since it has been discovered that they interact negatively with cellulase, in the pH conditions of the present invention. Derivatives of the amine softening agents include the corresponding amine compounds. Such amine softening agents are disclosed in e.g. EP.A 0.026.528 and EP.1 0.120.528, and include in particular amines of the formula $R_1R_2R_3N$ where $R_1$ and $R_2$ are $C_6$ to $C_{20}$ alkyl chains, and $R_3$ is $C_1$ to $C_{10}$ alkyl chain or hydrogen.

The compositions herein are formulated at a pH in the range of from 6.5 to 9.5, measured as a 1% solution of the composition in distilled water. At this pH-range, the cellulases for use herein have their optimum performance.

The fabric-softening clay material

The compositions herein must contain a clay softening agent.
Such clay softening agents are well-known in the detergency patent literature and are in broad commercial use, both in Europe and in the United States. Included among such clay softeners are various heat-treated kaolins and various multi-layer smectites. Preferred clay softeners are smectite softener clays that are described in German patent document 2334899 and in U.K. patent 1,400,898, which can be referred to for details.

The most preferred clay fabric softening materials include those materials of bentonitic origin, bentonites being primarily montmorillonite type clays together with various impurities, the level and nature of which depends on the source of the clay material. Softener clays are used in the preferred compositions at levels of at least 1%, generally 1-20%, preferably 2-10%.

Optional ingredients

The compositions herein may contain, in addition to the essential ingredients, certain optional ingredients. For instance, it is preferred that through-the-wash detergent compositions contain a detergent builder and/or metal ion sequestrant. Compounds classifiable and well-known in the art as detergent builders include the nitrilotriacetates, polycarboxylates, citrates, water-soluble phosphates such as tri-polyphosphate and sodium ortho- and pyro-phosphates, and mixtures thereof. Metal ion sequestrants include all of the above, plus materials like ethylenediaminetetraacetate, the amino-polyphosphonates and a wide variety of other poly-functional organic acids and salts too numerous to mention in detail here. See U.S. Patent 3,579,454 for typical examples of the use of such materials in various cleaning compositions. Preferred polyfunctional organic acids species for use herein are citric acid, ethylene diamine tetramethyleneephosphonic acid, and diethylene triaminepentamethylenephosphonic acid.
A further class of detergency builder materials useful in the present invention are insoluble sodium alumino-silicates. The 1-10 micron size zeolite (e.g., zeolite A) builders disclosed in German patent 24.22.655 are especially preferred for use in low-phosphate or non-phosphate compositions. In general, the builder/sequestrant will comprise from 0.5% to 45% of the composition.

The compositions herein can also contain fatty acids, saturated or unsaturated, and the corresponding soaps. Suitable fatty acids, saturated or unsaturated, have from 10 to 18 carbon atoms in the alkyl chain. Preferred are unsaturated species having from 14 to 18 carbon atoms in the alkyl chain, most preferably oleic acid. The corresponding soaps can also be used. The optional fatty acid/soaps are used in levels up to 20%.

The compositions herein can also contain compounds of the general formula R-CH(COOH)CH₂(COOH) i.e. derivatives of succinic acid, wherein R is C₁₀-C₂₀ alkyl or alkenyl, preferably C₁₂-C₁₆, or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents.

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanolammonium salts.

Specific examples of succinate builders include: lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenyl succinate (preferred), 2-pentadecenyl succinate, and the like.

Also useful as builders in the present context are the compounds described in U.S. patent 4,663,071, i.e. mixtures
of tartrate monosuccinic acid and tartrate disuccinic acid in a weight ratio of monosuccinic to disuccinic of from 97:3 to 20:80, preferably 95:5 to 40:60.

Another optional ingredient is a bleaching agent. Preferred are peroxigen bleaching agents such as sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate and urea peroxyhydrate.

Bleach activators may be used in combination with the above peroxigen bleaching agents. Classes of bleach activators include esters, imides, imidazoles, oximes, and carbonates. In those classes, preferred materials include methyl o-acetoxy benzoates; sodium-p-acetoxy benzene sulfonates such as sodium 4-octanoyloxybenzene sulfonate; sodium-4-octanoyloxybenzene sulfonate, and sodium-4-decanoyloxybenzenesulfonate; biphenol diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

Other highly preferred peroxigen bleach activators which are disclosed in U.S. Patents 4,483,778 and 4,539,130, are alpha-substituted alkyl or alkenyl esters, such as sodium-4(2-chlorooctanoyloxy)benzene sulfonate, sodium 4-(3, 5, 5-trimethyl hexanoyloxy)benzene sulfonate. Suitable peroxycacids are also peroxigen bleach activators such as described in published European Patent Application 0 166 571, i.e., compounds of the general type RXA00H and RXAL, wherein R is a hydroxcarbyl group, X is a hetero- atom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

Enzymes other than cellulases, such as proteolytic, amyloytic, or lipolytic enzymes can be used in addition to
the cellulase herein.

Soil-release/soil-suspending agents can be present in the composition herein at levels typically from 0.1% to 10% by weight. In particular: alkoxylated polyamines suitable as clay-soil removal/anti-redemption agents can be used. These components, as well as their preparation, are disclosed in EP-PA 0 112 593, the disclosures of which are incorporated herein by reference.

It is to be understood that the term "polyamines" as used herein represents generically the alkoxyated polyamines, both in their amine form and in their quaternarized form. Such materials can conveniently be represented as molecules of the empirical structures with repeating units:

\[
\begin{align*}
\text{Amine form:} & \quad \left[ \text{N} \overset{\text{R}}{\text{R}} \right]_n \\
\text{and} \quad & \quad (\text{Alkoxy})_y
\end{align*}
\]

\[
\begin{align*}
\text{Quaternized form:} & \quad \left[ \text{N}^+ \overset{\text{R}}{\text{R}} \right]_n^x \\
& \quad (\text{Alkoxy})_y
\end{align*}
\]

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R\(^1\) may be a C\(_{1-20}\) hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably 10-20; n is an integer of at least 2, preferably 2-20, most preferably 3-5; and X\(^{-}\) is an anion such as halide or methylsulfate, resulting from the quaternization reaction.
The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene imines, i.e., the polymerized reaction product of ethylene oxide with ethylene-imine, having the general formula:

\[
(\text{EtO})\left[\text{N} - \text{CH}_2\text{CH}_2\right]_n \text{N} - (\text{EtO})_y
\]

wherein \(n\) is an integer of 3 to 5 and \(y\) is an integer of 10 to 20.

Soil suspending agents can also be selected from polyethylene glycols, of molecular weight 400 to 1000, polyacrylates, or copolymers of acrylic acid and maleic anhydride/acid.

The detergent compositions herein are preferably free of carboxymethylcellulose.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, optical brighteners, hydrotropes and gel-control agents, freeze-thaw stabilizers, bactericides, preservatives, suds control agents, bleach stabilizing agents.
EXPERIMENTAL PART

A granular detergent composition was prepared, according to the following table:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>% by weight</th>
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<tr>
<td>Sodium Linear C\textsubscript{12} alkyl benzene sulfonate</td>
<td>11.0</td>
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<tr>
<td>Sodium Tallow alkyl sulfate</td>
<td>5.0</td>
</tr>
<tr>
<td>Tallow alcohol ethoxylate (E011)</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>24.0</td>
</tr>
<tr>
<td>Bentonite clay</td>
<td>8.5</td>
</tr>
<tr>
<td>Soil suspending agent*</td>
<td>2.0</td>
</tr>
<tr>
<td>Proteolytic enzyme</td>
<td>0.9</td>
</tr>
<tr>
<td>Sodium sulfate, water, minors</td>
<td>up to balance</td>
</tr>
</tbody>
</table>

* copolymer of acrylic and maleic acid, MW 60.000 (sodium salt).

From the basic composition hereinafore, two compositions were prepared:

Composition A, to be used as reference, where cellulase granulates (1.79 % by weight of total composition) containing crude cellulase enzymes and cellulose, were dry-mixed with the rest of the composition.

Composition B, a composition according to the present invention, where cellulase granulates (1.79 % by weight of total composition) containing crude cellulase enzyme, cellulose, and a coating of polyethylene glycol (5 % weight level of granulates, MW 1500) and of calcium carbonate (10 % weight level of granulates).
In both compositions A and B, the cellulase was of the type described in U.S. 4,435,307 and its amounts were such as to give an activity of 68 CMCase activity units/g of composition.

Compositions A and B were compared for softness and fabric-care performance.

The design of the test was such as to compare softness of textile pieces laundered 4, 8 and 12 times (multi-cycle) each time with invention and reference composition.

The testing conditions were as follows:
- Product usage: 92 grams = 0.75% conc.
- Wash temperature: 40° C.
- 18 grains/gallon (0.31 g/l) water hardness (3:1 Ca/Mg ratio).

The washed and line dried swatches were compared by a panel of two expert judges, working independently, by a paired comparison technique using a 9-point Scheffe scale. Differences were recorded in panel score units (psu), positive being performancewise better. (*) indicate significant results, with least significant difference (LSD) calculated at 95% confidence.

The testing results were as follows:

<table>
<thead>
<tr>
<th>a) Softness (bath towels)</th>
<th>number of cycles</th>
<th>comp.B vs. comp.A</th>
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<tr>
<td></td>
<td>4</td>
<td>+ 0.38 psu</td>
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<tr>
<td></td>
<td>8</td>
<td>+ 1.00* psu</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>+ 0.75* psu</td>
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</table>
b) **Fabric appearance** (improved color and anti-pilling performance)

(average on main cotton items)

<table>
<thead>
<tr>
<th>number of cycles</th>
<th>comp. B vs. comp. A</th>
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<tr>
<td>4</td>
<td>+ 0.69* psu</td>
</tr>
<tr>
<td>8</td>
<td>+ 0.75* psu</td>
</tr>
<tr>
<td>12</td>
<td>+ 0.75* psu</td>
</tr>
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</table>

The effect of polyethyleneglycol coating alone was measured as well, and results indicated negative performance effect, thus showing that the positive effect on both softness and fabric appearance are due to the presence of the calcium carbonate.
CLAIMS

1. A particulate composition for the cleaning and softening of fabrics, containing a surface-active agent, a fabric-softening clay material, and cellulase granulates, characterized in, that said granulates contain from 1% to 50%, by weight of said granulates, of calcium carbonate.

2. A composition in accordance with claim 1, wherein the calcium carbonate is present at levels of from 5% to 15% by weight of the cellulase granulates.

3. A composition in accordance with claim 1, wherein the calcium carbonate is coated onto the cellulase granulates.

4. A composition in accordance with claim 1, wherein the cellulase is bacterial or fungal cellulase having a pH optimum of between 5 and 11.5.

5. A composition in accordance with claim 1, wherein the cellulase is an alkali cellulase having an optimum pH from 6.5 to 9.5.

6. A composition in accordance with claim 1, wherein the composition has a cellulase activity of from 5 to 1360 CMCase activity unit/gram of composition.

7. A composition in accordance with claim 1, which contains from 1% to 50% by weight of the cellulase granulates, and from 1% to 20% by weight of the fabric-softening clay material.
8. A composition in accordance with claim 1 wherein the cellulase granulates are present at a level of from 1.5% to 10% by weight, and the fabric-softening clay material is present at a level from 2% to 10% by weight.

9. A composition in accordance with claim 1 wherein the fabric-softening clay material is a bentonite clay.

10. A composition in accordance with claim 1 wherein the cellulase granulates are free of titanium dioxide and magnesium silicate.

11. Cellulase granulates for use in the composition of claim 1, characterized in that they contain from 1% to 50%, by weight, of calcium carbonate.

12. Cellulase granulates according to claim 11, wherein the calcium carbonate is present at levels of from 5% to 15% by weight.

13. Cellulase granulates according to claim 11 which have the calcium carbonate coated onto them.

14. Cellulase granulates according to claim 11, wherein the cellulase is bacterial or fungal cellulase having a pH optimum of between 5 and 11.5.

15. Cellulase granulates according to claim 15, wherein the cellulase is an alkali cellulase having an optimum pH from 6.5 to 9.5.

16. Cellulase granulates according to claim 11 which are free of titanium oxide and magnesium silicate.
INTERNATIONAL SEARCH REPORT

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC: C 11 D 3/386; C 11 D 3/12

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System | Classification Symbols
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IPC | C 11 D; C 12 N

Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>Y</td>
<td>EP, A, 0177165 (UNILEVER) 9 April 1986 see the whole document cited in the application</td>
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<td>Y</td>
<td>GB, A, 2167758 (SHOWA DENKO K.K.) 4 June 1986 see claims 1,3,6,7; page 2, lines 39-43,78-93</td>
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IV. CERTIFICATION

Date of the Actual Completion of the International Search: 6th March 1989
Date of Mailing of this International Search Report: 10.04.89
International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: P.C.G. VAN DER PUTTEN
This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/03/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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