



(1) Publication number: 0 383 828 B1

# (12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 20.01.93 Bulletin 93/03

(51) Int. CI.5: C11D 3/386, C11D 3/12

(21) Application number: 89900022.8

(22) Date of filing: 18.11.88

86 International application number : PCT/DK88/00189

87) International publication number : WO 89/04862 01.06.89 Gazette 89/12

# 64) DETERGENT COMPOSITIONS CONTAINING CELLULASE GRANULATES.

(30) Priority: 19.11.87 GB 8727081

(43) Date of publication of application : 29.08.90 Bulletin 90/35

(45) Publication of the grant of the patent: 20.01.93 Bulletin 93/03

Designated Contracting States:
 AT BE CH DE FR GB IT LI LU NL SE

66) References cited:
EP-A- 0 170 360
EP-A- 0 177 165
GB-A- 2 167 758
Chemical Abstracts, volume 105, no. 26, December 1986, (Columbus, Ohio, US), see page 119, abstract 228963p

73 Proprietor: NOVO NORDISK A/S
Novo Allé
DK-2880 Bagsvaerd (DK)
Proprietor: THE PROCTER & GAMBLE
COMPANY
One Procter & Gamble Plaza
Cincinnati Ohio 45202 (US)

(72) Inventor: JENSEN, Poul, Erik
Lathyrusvej 3
DK-3450 Alleroed (DK)
Inventor: DE MARTELAERE, Dirk
Tervuursevest 120
B-3000 Leuven (BE)

(74) Representative: Canonici, Jean-Jacques et al Procter & Gamble European Technical Center N.V. Temselaan 100 B-1853 Strombeek-Bever (BE)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

### Description

### Technical field

5

15

20

25

30

35

40

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.

## 10 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-A-2,094,826, or Japanese patent 57108-199.

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

EP-A 0 120 528 teaches alkaline softening detergent compositions comprising a synergistic mixture of a water-insoluble C<sub>10</sub>-C<sub>26</sub> 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.

Such granulates are disclosed in e.g. EP-A-170 360 and U.S.-A-4,435,307, which mention 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.

Calcium-carbonate has been disclosed as colorant for laundry detergent enzyme granulates in GB-A-2,167,758 and in Japan Kokai JP 61,107,935.

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 granulate containing a water-insoluble salt of calcium.

## Summary of the Invention

45

50

55

The present invention relates to granular detergent compositions containing a fabric-softening clay material, and cellulase 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-sé.

# **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

5

10

15

20

25

35

40

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

Suitable cellulase are disclosed in U.S.-A-4,435,307, GB-A-2.095.275, DE-OS-2.247.832, and EP-A 0 220 016.

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 ferrocyanide 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 CMCase unit is defined as the amount of enzyme which forms per minute an amount of reducing carbohydrate equivalent to 10<sup>-6</sup> 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 but 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 is present in the cellulase granulates, at levels of from 1% to 50%, preferably 5% to 15% by weight, of the granulates.

Calcium carbonates of a particle size range from 1 to 10  $\mu m$  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 Britisch 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

55

50

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 sulphates and sulphonates, alkyl phenol polyethoxy ether sulphates, 2-acyloxy-alkane-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 - CH<sub>2</sub>CH<sub>2</sub>O- groups per molecule, especially from 10 to 16 carbon atoms in the alkyl chain and an average of from 1 to 6 -CH<sub>2</sub>CH<sub>2</sub>O-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 sultones 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 -CH<sub>2</sub>CH<sub>2</sub>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)  $C_{10}$ - $C_{20}$  primary and secondary alcohol ethoxylates and  $C_6$ - $C_{10}$  alkylphenol ethoxylates.  $C_{14}$ - $C_{18}$  linear primary alcohols condensed with from seven to thirty moles of ethylene oxide per mole of alcohol are preferred, examples being  $C_{14}$ - $C_{15}$  (EO)<sub>7</sub>,  $C_{16}$ - $C_{18}$  (EO)<sub>25</sub> and especially  $C_{16}$ - $C_{18}$  (EO)<sub>11</sub>.

Cationic co-surfactants which can be used herein, include water-soluble quaternay ammonium compounds of the form  $R_4R_5R_6R_7N^+X^-$ , wherein  $R_4$  is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and  $R_5$ ,  $R_5$  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 compound include  $C_{12}$ - $C_{14}$  alkyl trimethyl ammonium chloride and cocoalkyl trimethyl ammonium methosulfate.

The compositions of the invention should be 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.A 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 composition herein should be 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 cellulase for use herein have their optimum performance.

## The fabric-softening clay material

10

20

25

40

45

50

55

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 23 34 899 and in U.K. patent 1,400,898.

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 compositions at levels of 1-20 %, pre-

ferably 2-10 % by weight of the composition.

### Optional ingredients

5

10

15

20

25

30

35

40

50

55

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 polyfunctional organic acids and salts too numerous to mention in detail here. U.S. Patent 3.579.454 contains 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 tetramethylenephosphonic acid, and diethylene triaminepentamethylenephosphonic acid.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates. The 1-10  $\mu$ m 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. Suitably 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)CH<sub>2</sub>(COOH), i.e. derivatives of succinic acid, wherein R is  $C_{10}$ - $C_{20}$  alkyl or alkenyl, preferably  $C_{12}$ - $C_{16}$ , 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) and 2-pentadecenyl succinate.

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 peroxygen 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 peroxygen 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; bisphenol diacetate; tetra acetyl ethylene diamine; tetra acetyl hexamethylene diamine; tetra acetyl methylene diamine.

Other highly preferred peroxygen 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 peroxyacids are also peroxygen bleach activators such as described in published European Patent Application 0 166 571, i.e., compounds of the general type RXAOOH and RXAL, wherein R is a hydroxycarbyl group, X is a heteroatom, A is a carbonyl bridging group and L is a leaving group, especially oxybenzenesulfonate.

Enzymes other than cellulases, such as proteolytic, amylolytic, 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-redeposition agents can be used. These components, as well as their preparation, are disclosed in EP-A 0 112 593.

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

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms;  $R^1$  may be a  $C_1$ – $C_{20}$  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 ethyline-imine, having the general formula:

wherein n in 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**

20

25

30

35

40

45

50

55

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

6

	<u>Ingredients</u>	% by weight
5	Sodium Linear C <sub>12</sub> alkyl benzene sulfonate	11.0
	Sodium Tallow alkyl sulfate	5.0
	Tallow alcohol ethoxylate (E011)	0.3
10	Sodium tripolyphosphate	24.0
10	Bentonite clay	8.5 •
	Soil suspending agent*	2.0
15	Proteolytic enzyme	0.9
	Sodium sulfate, water, minors	up to balance
20	* copolymer of acrylic and maleic acid, MW	60.000
	(sodium salt).	

From the basic composition hereinabove, two compositions were prepared:

<u>Composition A</u>, 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.-A-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 (multicycle) 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:

45	<ul><li>a) <u>Softness</u></li></ul>	number of cycles	comp.b vs. comp.A
	(bath towels)	4	+ 0.38 psu
		8	+ 1.00* psu
50		12	+ 0.75* psu

55

25

30

35

40

b) Fabric appearance (improved color and anti-pilling performance)

(average on main cottom items)

number	of cycles	comp.B	vs. comp. A
	4	+	0.69* psu
	8	+	0.75* psu
	12	+	0.75* psu

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**

20

5

10

1. A particulate composition for the cleaning and softening of fabrics, containing from 1% to 50% by weight of a surface-active agent, from 1% to 20% by weight of a fabric-softening clay material, and from 1% to 50% by weight of cellulase granulates, characterized in that said granulates contain from 1% to 50%, by weight of said granulates, of calcium carbonate.

25

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.

30

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

optimum pH of between 5 and 11.5.

A composition in accordance with claim 1, wherein the cellulase is bacterial or fungal cellulase having an

35

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

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.

40

7. 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.

45

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

-

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

--

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

50

**11.** Cellulase granulates according to claim 10, wherein the calcium carbonate is present at levels of from 5% to 15% by weight.

55

**13.** Cellulase granulates according to claim 20, wherein the cellulase is bacterial or fungal cellulase having an optimum pH of between 5 and 11.5.

12. Cellulase granulates according to claim 10 which have the calcium carbonate coated onto them.

- **14.** Cellulase granulates according to claim 13, wherein the cellulase is an alkali cellulase having an optimum pH from 6.5 to 9.5.
- 15. Cellulase granulates according to claim 10 which are free of titanium oxide and magnesium silicate.

5

30

35

45

50

55

### Patentansprüche

- 1. Teilchenförmige Zusammensetzung zur Reinigung und Weichmachung von Geweben, enthaltend 1 Gew.-% bis 50 Gew.-% eines grenzflächenaktiven Mittels, 1 Gew.-% bis 20 Gew.-% eines gewebeweichmachenden Tonmaterials und 1 Gew.-% bis 50 Gew.-% an Cellulasegranulaten, dadurch gekennzeichnet, daß die genannten Granulate 1 % bis 50 %, bezogen auf das Gewicht der genannten Granulate, an Calciumcarbonat enthalten.
- Zusammensetzung nach Anspruch 1, worin das Calciumcarbonat in Mengen von 5 Gew.-% bis 15 Gew.-der Cellulasegranulate vorliegt.
  - 3. Zusammensetzung nach Anspruch 1, worin die Cellulasegranulate mit Calciumcarbonat beschichtet sind.
- 4. Zusammensetzung nach Anspruch 1, worin die Cellulase eine Cellulase aus Bakterien oder Pilzen mit einem Optimum bei einem pH-Wert von 5 bis 11,5 ist.
  - **5.** Zusammensetzung nach Anspruch 1, worin die Cellulase eine Alkali-cellulase mit einem Optimum bei einem pH-Wert von 6,5 bis 9,5 ist.
- 25 **6.** Zusammensetzung nach Anspruch 1, worin die Zusammensetzung eine Cellulaseaktivität von 5 bis 1360 CMCase-Aktivitäts-Units/Gramm an Zusammensetzung aufweist.
  - 7. Zusammensetzung nach Anspruch 1, worin die Cellulasegranulate in einer Menge von 1,5 Gew.-% bis 10 Gew.-% vorhanden sind und das gewebeweichmachende Tonmaterial in einer Menge von 2 Gew.-% bis 10 Gew.-% vorliegt.
  - 8. Zusammensetzung nach Anspruch 1, worin das gewebeweichmachende Tonmaterial ein Bentonitton ist.
  - 9. Zusammensetzung nach Anspruch 1, worin die Cellulasegranulate von Titandioxid und Magnesiumsilicat frei sind.
  - **10.** Cellulasegranulate für die Verwendung in der Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie 1 Gew.-% bis 50 Gew.-% an Calciumcarbonat enthalten.
- **11.** Cellulasegranulate nach Anspruch 10, worin das Calciumcarbonat in Mengen von 5 Gew.-% bis 15 Gew.
  40 % vorhanden ist.
  - 12. Cellulasegranulate nach Anspruch 10, welche mit dem Calciumcarbonat beschichtet sind.
  - **13.** Cellulasegranulate nach Anspruch 10, worin die Cellulase eine Cellulase aus Bakerien oder Pilzen mit einem Optimum bei einem pH-Wert von 5 bis 11,5 ist.
    - **14.** Cellulasegranulate nach Anspruch 13, worin die Cellulase eine Alkalicellulase mit einem Optimum bei einem pH-Wert von 6,5 bis 9,5 ist.
  - 15. Cellulasegranulate nach Anspruch 10, welche von Titanoxid und Magnesiumsilicat frei sind.

### Revendications

1. Composition particulaire pour nettoyer et adoucir les tissus, contenant de 1% à 50% en poids d'un agent tensioactif, de 1% à 20% en poids d'une substance à base d'argile adoucissant les tissus et de 1% à 50% en poids de granulats de cellulase, caractérisée en ce que lesdits granulats contiennent de 1% à 50%, en poids desdits granulats, de carbonate de calcium.

- 2. Composition selon la revendication 1, dans laquelle le carbonate de calcium est présent en proportions de 5% à 15% du poids des granulats de cellulase.
- 3. Composition selon la revendication 1, dans laquelle le carbonate de calcium enrobe les granulats de cellulase.
  - **4.** Composition selon la revendication 1, dans laquelle la cellulase est une cellulase bactérienne ou fongique ayant un pH optimal compris entre 5 et 11,5.
- 5. Composition selon la revendication 1, dans laquelle la cellulase est une cellulase alcaline ayant un pH optimal de 6,5 à 9,5.
  - 6. Composition selon la revendication 1, dans laquelle la composition a une activité de cellulase de 5 à 1360 unités d'activité de CMCase/gramme de composition.
- 7. Composition selon la revendication 1, dans laquelle les granulats de cellulase sont présents en une proportion de 1,5% à 10% en poids et la substance à base d'argile adoucissant les tissus est présente en une proportion de 2% à 10% en poids.
- **8.** Composition selon la revendication 1, dans laquelle la substance à base d'argile adoucissant les tissus est une argile de type bentonite.
  - **9.** Composition selon la revendication 1, dans laquelle les granulats de cellulase sont exempts de dioxyde de titane et de silicate de magnésium.
- 25 **10.** Granulats de cellulase utilisables dans la composition de la revendication 1, caractérisés en ce qu'ils contiennent de 1% à 50%, en poids, de carbonate de calcium.
  - **11.** Granulats de cellulase selon la revendication 10, dans lesquels le carbonate de calcium est présent en proportions de 5% à 15% en poids.
- 30 **12.** Granulats de cellulase selon la revendication 10, qui sont enrobés de carbonate de calcium.
  - **13.** Granulats de cellulase selon la revendication 10, dans lesquels la cellulase est une cellulase bactérienne ou fongique ayant un pH optimal compris entre 5 et 11,5.
- 35 **14.** Granulats de cellulase selon la revendication 13, dans lesquels la cellulase est une cellulase alcaline ayant un pH optimal de 6,5 à 9,5.
  - **15.** Granulats de cellulase selon la revendication 10, qui sont exempts d'oxyde de titane et de silicate de magnésium.

45

40

50

55