

(1) Publication number: 0 652 282 A1

12

EUROPEAN PATENT APPLICATION

(21) Application number : 94304403.2

(51) Int. CI.⁶: **C11D 3/12**, D06M 11/79

(22) Date of filing: 17.06.94

(30) Priority: 16.07.93 GB 9314846

(43) Date of publication of application : 10.05.95 Bulletin 95/19

84 Designated Contracting States : CH DE ES FR GB IT LI NL SE

(1) Applicant: UNILEVER PLC Unilever House Blackfriars London EC4P 4BQ (GB)

(84) GB

71) Applicant : UNILEVER N.V. Weena 455 NL-3013 AL Rotterdam (NL)

(84) CH DE ES FR IT LI NL SE

72) Inventor: Azoz, Nazal Essa Naom, Unilever Research Port Sunlight Lab., Quarry Road East, Bebington Wirral, Merseyside L63 3JW (GB) Inventor: Prescott, John Andrew, Unilever Research Port Sunlight Lab., Quarry Road East, Bebington Wirral, Merseyside L63 3JW (GB) Inventor : Bishop, David Paul White Lodge, 104 Birkenhead Road, Meols Wirral, Merseyside L47 0LE (GB)

(74) Representative: Ford, Michael Frederick et al MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

- (54) Use of fabric treatment compositions.
- 57) The invention relates to the second chemical use of a fabric softening clay for the control and prevention of fibre damage caused by washing and use of fabrics.

EP 0 652 282 A1

The invention relates to the use of a fabric softening clay for control and prevention of fibre damage caused by washing and use of fabrics.

A typical wash will include some fabric containing cellulose based fibres. Abrasion of cellulose based fibres under wet conditions results in cotton fibre fibrillation whereby the cotton fibres are gradually broken down into their component fibrils and into fibrillar sheets. Such fibrillation is an important mechanism by which fabrics are damaged during wash processes. Alternatively abrasion of cellulose fibres occurs when a garment is dry. This abrasion or dry wear takes the form of the fibre cracking.

The surfaces of damaged fabrics scatter light to a greater extent than undamaged fabrics and the scattering causes dulling of fabric colours. Ultimately the damage will result in mechanical disintegration of the fibre and the consequent failure of cotton garments. The main causes of fibrillation have been found to be agitation (rubbing) of the fibres when wet. Dry friction can also cause fibre damage, as the fibre can crack.

10

20

25

30

35

40

45

50

55

WO 89/04862 relates to a detergent composition for cleaning and softening fabrics in which cellulase granulates containing calcium carbonate are used in certain combinations with a fabric softening clay to wash cotton swatches. A composition comprising cellulase and clay is said to improve the appearance of the cotton fabric by improved colour and anti-pilling performance. These improvements are probably due to the action of cellulase on cotton which is a cellulosic fibre.

GB 1 400 898 relates to the use of certain clays in detergent compositions for imparting a softening benefit to fabrics washed therewith. (No pilling prevention or control is mentioned.)

Our copending applications GB 9218342.5 and GB 9218330.0 disclose the use of fabric softening composition containing quaternary ammonium compounds for the use as fabric damage inhibitors or reducers.

It is an object of the present invention to provide a method of preventing damage to fibres in particular cellulose fibres eg. cotton and viscose and thereby to increase the life of garments containing the fibres.

According to the invention there is provided the use of a clay as a fibre damage inhibitor.

Throughout this specification the term inhibitor includes a component which confers protective care or protection on a fibre. In particular it encompasses those materials which reduce the damage to the fibre which would otherwise occur during the course of wearing and washing a garment.

Damage of fibres can take place in several ways. The use of a fabric softening clay particularly addresses the problem of dry damage and fibrillation. Dry damage causes cracking of the fibres and is shown in Figure 2. Fibrillation is the splitting of the fibres to form fibrils and is shown by Figure 3.

Examples of suitable clays for use in the present invention include various heat treated kaolins and various multi-layer smectites eg. bentonites. Preferred clays are softening clays such as smectite softener clays as described in GB 1 400 898, EP 350 288 and EP 0 297 673.

Montmorillonite clays are especially preferred eg. Volclay. Softening clays are used in the preferred compositions at levels of at least 0.1%, generally 1-30%, preferably 2-10% by weight.

The invention further provides the use of a fabric softening clay in a fabric conditioning composition for the prevention of fibre damage and to protect fibres.

This aspect of the invention has the advantage that the use of the fabric softening clay can be carried out as part of a rinsing process giving a desirable overall effect of softening and fibre damage control or prevention. Further more the clay when deposited in this manner can protect the fibres after the rinsing process and during wear and use of articles and the protection conferred can be carried over to the next wash.

The fabric softening clays may be used in admixture with one or more fabric softening materials such as cationic fabric softeners or amine materials. Examples of suitable cationic fabrics softeners include substantially water insoluble quaternary ammonium compounds such as for instance dihardened tallow dimethyl ammonium chloride, imidazolonium salts and similar di (long-chain) quaternaries and ester-linked quaternaries as for instance disclosed in EP 239 910, US 3 915 867 and US 4 137 180.

Examples of amine materials include tertiary amines and those disclosed in EP 0 199 383 and EP 0 345 842.

The fabric softening composition can also contain fatty acids for example C_8 - C_{24} alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C_{16} - C_{18} fatty acids. Preferably the fatty acid is non-saponified, more preferably the fatty acid is free; for example oleic acid, lauric acid or tallow fatty acid.

The level of cationic for use in the fabric softening composition according to the invention may constitute from 5 to 97 wt% of the total wt% of the composition.

The compositions of the invention preferably have a pH of more than 2, more preferably between 2 and 5.

The compositions can also contain one or more optional ingredients, selected from non-aqueous solvents, pH buffering agents, perfumes, perfume carriers, fluorescers, colorants, hydrotropes, anti-foaming agents, anti-redeposition agents, enzymes, freeze-thaw stabilisers, optical brightening agents, opacifiers, anti-

shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-oxidants, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids.

The composition may also contain nonionic fabric softening agents such as lanolin and derivatives thereof. The invention further provides the use of a fabric softening clay in a composition comprising a detergent active for the prevention of fibre damage or to protect fibres. The use of softening clays may further confer a softening benefit, in such detergent compositions.

The detergent active material may be selected from soaps, non-soap anionic, nonionic, zwitterionic and amphoteric synthetic detergent active materials and optionally one or more fabric softening materials.

Many suitable detergent compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Anionic surfactants useful in the present invention include: Linear alkyl sulphonates. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8 - C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8 - C_{18}) fatty alcohol-alkylene oxides, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8 - C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and SO_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly SO_3 and then neutralising and hydrolysing the reaction product. Preferred anionic detergent compounds are sodium (SO_3 and the neutralising and hydrolysing the reaction product. Preferred anionic detergent compounds are sodium (SO_3 alkyl benzene sulphonates and sodium (SO_3 alkyl sulphates. Directly esterified isethionates may also be used.

Suitable nonionic compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6 - C_{22}) phenols-ethylene oxide condensates, generally up to 25 EO, i.e. up to 25 units of ethylene oxide per molecule, the condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally up to 40 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamide. Other so-called nonionic detergent compounds include alkyl polyglycosides, long tertiary amide oxides, glucamines, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Amounts of amphoteric or zwitterionic detergent compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used it is generally in small amounts.

The effective amount of the detergent active or fabric softening compound or compounds used in the composition of the present invention is generally in the range of up to 50%, preferably up to 40% by weight, most preferably not more than 30% by weight of the composition. Preferably the level is above 1%, most preferably more than 2%.

Compositions of the invention may include detergency builder to improve the efficiency of the detergent active, in particular to remove calcium hardness ions from the water. The builder material may be selected from inorganic precipitating builders materials (such as alkali metal carbonates, bicarbonates, borates, orthophosphates and silicates), sequestering builder materials (such as alkali metal pyrophosphates, polyphosphates, amino polyacetates, phytates, polyphosphonates, aminopolymethylene phosphonates and polycarboxylates), ion-exchange builder materials (such as zeolites and amorphous alumino-silicates), organic precipitating builder materials (such as those having the formula (I):

$$R_1 - X$$
 $CH_2)_m Z$
 $CH_2)_m Z$

55

5

10

15

20

25

30

35

40

45

50

wherein: R_1 is C_{10} - C_{24} alkyl or alkenyl, or an arylalkyl or alkylaryl group of equivalent chain length; X is CH, CR_2 , N or CON; R_2 is C_1 - C_3 alkyl; Z is COOY or SO_3Y ; Y is hydrogen or a solubilising cation, preferably alkali

metal and especially sodium; and n and m, which may be the same or different, are O or integers from 1 to 4, or mixtures of any one or more of these materials. Preferred examples of builder materials include sodium tripolyphosphate, mixtures thereof with sodium orthophosphate, sodium carbonate, mixtures thereof with calcite as a seed crystal, citrates, zeolite and the sodium salt of nitrili- triacetic acid. Among the Zeolites that find application in the present invention there may be mentioned: Zeolite A and X and mixtures thereof, particularly Zeolite 4A. Also of interest is Zeolite P described and claimed in EP0384070.

The level of such builder material in the compositions of the invention may from 2 to 80% by weight, preferably from 7% to 70% by weight and most preferably from 14% to 60% by weight.

Compositions comprising a detergent active according to the invention preferably are neutral or slightly alkaline when added to water at a concentration of 1% by weight at 25°C. Neutral compositions are especially preferred for wool wash use.

Apart from the components already mentioned, a composition of the invention can contain any of the conventional additives in the amount in which such additives are normally employed in fabric washing detergent compositions. Optional additives include the lather boosters such as alkanolamides, particularly the monoethanolamides derivatives from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes including deodorant perfumes, enzymes such as cellulases, lipases, proteases and amylases, germicides and colourants.

The compositions may be in any convenient form such as bars, powders, flakes, pastes or liquids which may be aqueous or non-aqueous and structured or unstructured.

The detergent compositions may be prepared in any way appropriate to their physical form such as by drymixing the components, co-agglomerating them or dispersing them in a liquid carrier.

The invention will now be illustrated by the following non-limiting examples and with reference to the accompanying drawings of which:

Figure 1 is a diagrammatic representation of the fibre damage test apparatus used.

Figure 2 is a photograph of fibre damage caused by dry abrasion.

Figure 3 is a photograph of fibrillation caused by wet abrasion.

Figure 4 is a photograph of fibres washed without clay.

Figure 5 is a photograph of fibres washed with clay.

Figure 6 is a photograph of fibres rinsed with clay.

Figure 1 shows a yarn on yarn abrasion tester with a test yarn 1 comprising fibres. The two ends of the yarn are attached to metal links 2 and 3. Metal link 2 joins the yarn to a cord 4 which passes over a first upper yarn guide pulley 4A and is attached to a tensioning weight 5. Typically a 20g tensioning weight is used. The other end of the yarn is attached to a second cord 6 by the metal link 3. Between the metal links the yarn is twisted about itself in the test region 7 and is weighed down by passing the yarn around a lower yarn guide pulley 8. The second cord 6 passes over a second upper yarn guide pulley 9 and is attached to an electrically driven reciprocating means 10. A beaker 11 is provided for containing water or aqueous media used to test the yarn in wet conditions.

The test method consists of attaching the yarn to be tested to one of the metal links, passing the yarn around the lower yarn guide pulley 9 and then twisting the yarn around itself a predetermined number of times to form the region 7, before attaching it to the other metal link. If required, the beaker is filled with an aqueous test medium. The reciprocating means is then switched on. A record is kept of the number of oscillations of the reciprocating means before failure. In each of the following examples the test was repeated a number of times and very high or low results discarded before a statistical analysis was made of the remaining date. (Very high or low results are due to defective fibres).

Comparative examples are illustrated by a letter. Examples of the invention are illustrated by a number.

Examples 1, 2, 3, A, B and C

100% extracted cotton yarns were subjected to the following treatment:

55

50

10

20

25

30

35

40

45

	Example A	Soaked in cold Wirral water at room
-		temp.
5	Example 1	Soaked in water + clay (0.5 g/l of Na)
		Montmerillonite powder)
	Example B	$ exttt{Washed}^{\star}$ with New Persil Automatic
10		Biological - no clay
	Example 2	\mathtt{Washed}^{\star} with \mathtt{New} \mathtt{Persil} $\mathtt{Automatic}$
		Biological with clay (0.5 g/l of Na
15		Montmerillonite powder)
70	Example C	Washed in New Persil Automatic * - non
		biological
	Example 3	Washed in New Persil Automatic * - non
20		biological with clay (0.5g water/1 of
		Na montmerillonite powder) and rinsed 4
		times with clay in the final rinse
25		(0.5g/l of Na montmerillonite).
*	The "washed"	samples were agitated for 15 minutes at
		samples were agitated for 15 minutes at ne recommended dose of a washing powder
* 30	50°C using th	
	50°C using the sold under the	ne recommended dose of a washing powder
	50°C using the sold under the Biological of the solution of th	ne recommended dose of a washing powder ne trade mark "New Persil automatic-
	50°C using the sold under the Biological of the solution of th	ne recommended dose of a washing powder ne trade mark "New Persil automatic- or New Persil Automatic Non Biological and
30	50°C using the sold under the Biological " of having the ge	ne recommended dose of a washing powder ne trade mark "New Persil automatic- or New Persil Automatic Non Biological and
30	50°C using the sold under the Biological " of having the general wt%	ne recommended dose of a washing powder ne trade mark "New Persil automatic-or New Persil Automatic Non Biological and eneral composition:
30	50°C using the sold under the Biological " of having the general with the solution of the solu	ne recommended dose of a washing powder ne trade mark "New Persil automatic-or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate
30 35	50°C using the sold under the Biological" of having the general way 6.0	ne recommended dose of a washing powder ne trade mark "New Persil automatic-or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate Nonionic 7EO
30 35	50°C using the sold under the Biological" of having the general ways and the sold ways are sold with the sold ways are sold ways are sold with the sold ways are sold with the sold ways are sold ways	ne recommended dose of a washing powder ne trade mark "New Persil automatic-or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate Nonionic 7EO Nonionic 3EO
30 35 40	50°C using the sold under the Biological" of having the general ways and the sold with	ne recommended dose of a washing powder ne trade mark "New Persil automatic- or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate Nonionic 7EO Nonionic 3EO Sodium tripolyphosphate
30 35	sold under the Biological " of having the get with the sold with the sol	ne recommended dose of a washing powder ne trade mark "New Persil automatic- or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate Nonionic 7EO Nonionic 3EO Sodium tripolyphosphate perborate tetrahydrate
30 35 40	sold under the Biological " of having the get with the sold with the sol	ne recommended dose of a washing powder ne trade mark "New Persil automatic- or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate Nonionic 7EO Nonionic 3EO Sodium tripolyphosphate perborate tetrahydrate sodium sulphate
30 35 40	sold under the Biological " of having the get with the second	ne recommended dose of a washing powder ne trade mark "New Persil automatic- or New Persil Automatic Non Biological and eneral composition: Alkyl benzene sulphonate Nonionic 7EO Nonionic 3EO Sodium tripolyphosphate perborate tetrahydrate

The yarns were then rinsed for 5 minutes at room temperature. Four rinses were applied.

50

55

After treatment the yarns were allowed to dry for 24 hours at room temperature. They were then individually abraded on the yarn on yarn abrasion tester. Abrasion tests were carried out dry, in their original treatment solutions and in water. All tests were carried out using cold Wirral water at room temperature. Table 1 shows the mean number of cycles before 16 samples of yarn failed in an abrasion test.

Table 1

Example **Test Conditions** Dry **Original Solution** In water 473 Α 1606 1656 2230 1 782 1744 В 484 1498 1498 2 530 1735 1584 С 660 1360 3 1178 1845

15

20

5

10

The difference in the number of cycles between the samples treated with clay according to the present invention and the other samples is significant in all test conditions.

In order to check whether the differences were statistically significant F and T tests were performed on the data. It can be concluded from this analysis that the use of clay gives reduced fibre damage during the dry abrasion that would occur when a garment is being worn and prevents damage during the wash.

Example 3 shows that further fibre damage is reduced if clay is present in both the wash and the final rinse.

Examples 4, 5 and D

25

30

35

Example 4 was treated with Na Montmerillonite clay and washed in New Persil Automatic Biological. Example 5 was treated with Na Montmerillonite clay in an aqueous solution (tg washing powder per L). (This treatment simulates adding clay during the rinse).

Example D was not treated and washed with New Persil Automatic Biological

A photograph of Example D is shown in Figure 4,

Figure 5 is a photograph of Example 4,

Figure 6 is a photograph of Example 5.

The photograph show that clay mitigates fibre damage when added in a rinse cycle or during the main wash.

Furthermore it can be seen that clay can reduce fibre damage/fibrillation and thus increase yarn life time more effectively when it is applied to the last rinse.

Claims

40

- 1. Use of clay as a fibre damage inhibitor.
- 2. Use of a fabric softening clay as a fibre damage inhibitor or fibre protector.
- 45 **3.** Use of a fabric softening clay in a fabric conditioning composition for the prevention of fibre damage or to protect fibres.
 - **4.** Use of a fabric softening clay in a composition comprising a detergent active for the prevention of fibre damage or to protect fibres.

50

- **5.** Use of a clay according to any preceding claim in which the fibre damage comprises of fibre fibrillation or dry damage.
- 6. Use of a clay according to any preceding claim in which the fibre comprises cotton.

55

7. Use of a clay according to any preceding claim in which the clay is selected from the group consisting Montmorillonite and Hectorite.

	8.	Use of a fabric softening clay according to Claim 2 in which the level of the fabric softening clay is in the range from 2% to 10% of the total wt% of the composition.
5	9.	Use of a fabric softening clay according to claim 3 in which the level of the fabric softening clay is in the range from 5 wt% to 15 wt% of the total wt% composition.
10		
15		
20		
25		
30		
35		
40		
45		
50		
55		

Schematic Diagram of Yarn-on-Yarn Abrasion [ester

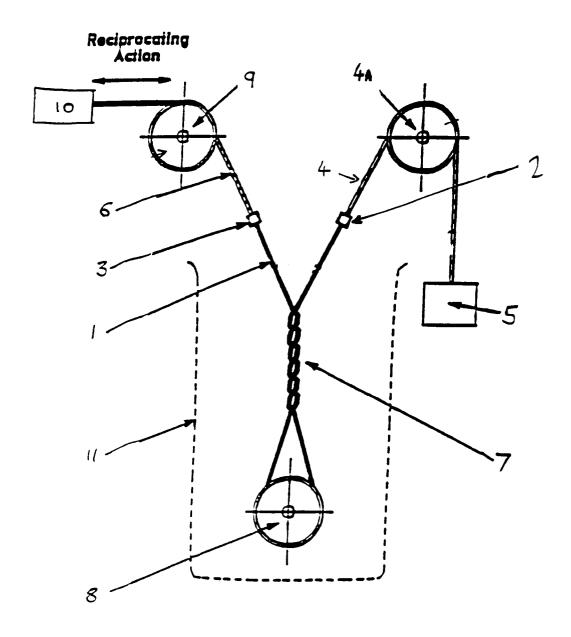


Figure 2



Figure 3



Figure 4



Figure 5

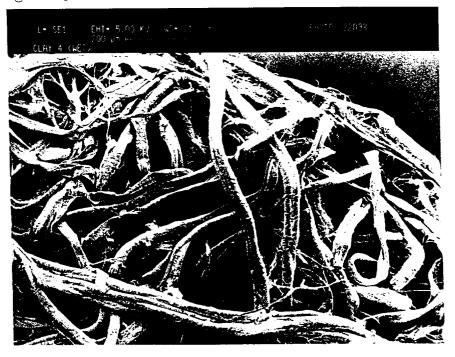


Figure 6





EUROPEAN SEARCH REPORT

Application Number EP 94 30 4403

Category	Citation of document with of relevant	n indication, where appropriate, passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 073 996 (BE * abstract * * column 3, line 5	1-3,5-7	C11D3/12 D06M11/79	
(US-A-3 063 784 (G. * column 1, line 2	O. ETCHINSON ET. AL.	.) 1-3,5,7	
(EP-A-0 183 222 (G. * page 3, line 20 * page 4, line 15 * page 7, line 31	- line 32 *	1-3,5,6	
	CORPORATION)	BUSHIKI KAISHA J. F. page 4, line 10 *	1,2	
	WO-A-92 07927 (THE COMPANY) * page 4 - page 6 * page 17, line 15	*	1-4,7-9	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
	EP-A-O 614 966 (UN * page 2, line 1 -	ILEVER PLC) page 3, line 32 *	1-4	C11D D06M
	The present search report has			
	Place of search THE HAGUE	Date of completion of the sear 8 March 1995		Exeminer terer, M
C X : partie Y : partie	ATEGORY OF CITED DOCUMI cularly relevant if taken alone cularly relevant if combined with ar ment of the same category	ENTS T: theory or p E: earlier pate after the fi nother D: document	orinciple underlying the sent document, but publis	invention