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 (3) Priority : 10.03.93 GB 9304898 (4) Date of publication of application : 14.09.94 Bulletin 94/37 (8) Designated Contracting States : CH DE ES FR GB IT LI NL SE (7) Applicant : UNILEVER PLC Unilever House Blackfriars London EC4P 4BQ (GB) (84) GB (7) Applicant : UNILEVER N.V. Weena 455 NL-3013 AL Rotterdam (NL) (84) CH DE ES FR IT LI NL SE 	 (72) Inventor : Bishop, David Paul, Unilever Research Port Sunlight Lab., Quarry Road East, Bebington Wirral, Merseyside, L63 3JW (GB) Inventor : Prescott, Andrew John 25 Langdale Road, Bebington Wirral, Merseyside, L63 3AN (GB) (74) Representative : Fransella, Mary Evelyn et al Unilever PLC Patent Division Colworth House Sharnbrook Bedford MK44 1LQ (GB) 			

- (54) Use of a fabric softening clay.
- (57) Use of a fabric softening clay as an additive to reduce or prevent wash damage of woollen articles in a fabric washing composition comprising an anionic surfactant, a nonionic surfactant and a proteolytic enzyme.

This invention relates to the use of a fabric softening clay as an additive in a fabric washing composition comprising an anionic surfactant, a nonionic surfactant and a proteolytic enzyme.

In GB 1 400 898 (Procter & Gamble/STORM) a detergent and softening composition is taught which includes a smectite clay containing material having a cation exchange capacity of at least 50 meq/100g, together 5 with a detergent active material. Enzymes are suggested as a possible additive to the composition.

Recently it has become the practice to incorporate more enzymes in fabric washing compositions so that the compositions can be used at lower temperatures to save energy and reduce the damage to clothes caused by high temperature washing. There is also a trend towards washing woollen garments in the washing machine, even if they are marked 'hand wash only'. The damage caused by washing wool in a fabric washing composition

- containing high levels of proteolytic enzyme can be considerable in terms of weight loss of the fabric, shrinkage 10 and eventual disintegration of the garment by formation of holes. According to the present invention there is provided the use of from 2 to 30% by weight of a fabric softening clay as an additive to reduce or prevent wash damage of woollen articles in a fabric washing composition comprising an anionic surfactant, a nonionic surfactant and a proteolytic enzyme. The advantage of such a use of a fabric softening clay is that the damage
- 15 to the woollen clothes may be considerably reduced without a reduction in the detergency of the fabric washing composition. It might be expected that if the clay were inhibiting the enzyme activity, then this would result in reduced detergency, especially of proteinaceous stains. Surprisingly this does not happen.

The clay may be added in the form of a granule comprising 10 to 30% by weight nonionic surfactant. Such a mode of addition is advantageous for a granular detergent composition because it enables the clay to be conveniently post-dosed to the formulation. The non-ionic provides for easy granulation of the clay.

Preferably the clay is selected from layered smectites and hectorites as these are the common naturally occurring fabric softening clays. Clay mineral containing materials useful in the present invention include dioctahedral and trioctahedral three layer smectite clays, ideally of the calcium and/or sodium montmorillonite type. For example PRASSA clay from Greece, GELWHITE from Texas USA, Willemse from South Africa and

25 VOLCLAY BC from Wyoming. The effectiveness of a clay containing material as a fabric softener will depend partly on the level of clay mineral in the material. Most preferably the clay is a bentonite such as a montmorillonite.

The composition may further comprises Lipolytic enzyme, such as Lipolase. The clay also prevents some damage to wool which may be attributable to such other enzymes.

Clay protection appears to be particularly beneficial if the pH of the composition in the wash is between 7.5 and 10.5, preferably between 9 and 10.

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 (C₈-C₁₈) alcohols produced for example from tallow or coconut oil, sodium and potassium

- 35 alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) 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 (C8-C18) fatty alcohol-alkylene oxides, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty 40 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 (Ca-C₂₀) with sodium bisulphite and those derived from reacting paraffins with SO₂ and Cl₂ 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 C₁₀-C₂₀ alpha-olefins, with SO₃ and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C11-C15) alkyl benzene 45
 - sulphonates and sodium (C₁₆-C₁₈) alkyl sulphates.

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Suitable nonionic surfactants 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, amide or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic

- 50 detergent compounds are alkyl (C₆-C₂₂) phenols-ethylene oxide condensates, generally up to 25 EO, i.e. up to 25 units of ethylene oxide on average 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 ethylenediamine. Other socalled nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine 55 oxides and dialkyl sulphoxides.
 - Mixtures of detergent compounds, for example mixed anionic or mixed anionic and nonionic compounds may be used in the detergent compositions, particularly in the latter case to provide controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines.

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 in compositions based on the much more commonly used synthetic anionic and/or nonionic detergent compounds.

- A detergency builder may also be present. This may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the suspension of the fabric softening clay material. The level of the detergency builder may be from 10% to 70% by weight, most preferably from 25% to 50% by weight.
- 10 Examples of detergency builders include precipitating builders such as the alkali metal carbonates (with or without seed crystals such as calcite), bicarbonates, ortho phosphates, sequestering builders such as the alkali metal tripolyphosphates or nitrilotriacetates, or ion-exchange builders such as the amorphous alkalimetal aluminosilicates or the zeolites.
- The clay material can be added in various physical forms. It may, for example, be spray-dried with other components of the formulation or it may be added separately. In the latter case the clay may be ground to a suitable size, say 5 to 2000 microns, or may be in the form of granulated fine particles optionally containing a binder such as an inorganic salt or a surfactant.

Proteolytic enzymes that may be used in the present invention include the Savinases, such as Savinase 6.0T (ex Novo), Opticlean (Solvay) and Maxacal (Ibis) also Alcalases such as Alcalase 2.34 LVX and Esperase

20 8.0 (Novo), Optimase (Solvay) and Maxatase (Ibis). Lipases and cellulases may also be included in the composition.

Apart from the components already mentioned, a detergent composition of the invention can contain any of the conventional additives in the amounts in which such additives are normally employed in fabric washing detergent compositions. Examples of these additives include additional fabric softening agents such as a ca-

 tionic fabric softening agent or a fatty amine. Further examples of these additives include the lather boosters such as alkanolamides, particularly the monoethanolamides derived 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 trichlorisyocyanuric acid, inorganic salts such as sodium sulphate, other fillers such as kaolin, and, usually present in very minor
 amounts, fluorescent agents, perfumes, other enzymes such as amylases, germicides and colorants.

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

Figure 1 is a photograph of lambs wool cloths washed in compositions with and without clay;

Figure 2 is a photograph of Botany wool cloths washed in compositions with and without clay; and

³⁵ Figure 3 is a photograph of Shetland wool cloths washed in compositions with and without clay.

Example 1

Fabric washing powders of the following compositions were prepared by conventional techniques. The clay nonionic granule used for composition B was prepared by aggregation and post dosed to the base powder. The base powder for composition B was the same as that for composition A except for the addition of the clay/nonionic granules.

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	Table 1			
		Composition A	Composition B	
5	Anionic	18.5	16.65	
	Nonionic	4.6	4.14	
	Savinase 6.0T	0.65	0.85	
10	Zeolite	35.9	32.31	
	Sodium carbonate	12.4	11.16	
	Polymer	4.4	3.96	
15	Sodium bicarbonate	4.0	3.6	
	Water	14.5	13.05	
	Lipolase 100T	0.30	0.27	
20	Minor Ingredients	4.75	4.275	
	Clay/nonionic	-	10	

In the following examples these compositions were used in a computer controlled Miele washing machine using a 40°C cotton programme. This programme was selected in order to show the damage effects of washing with a powder containing an enzyme more rapidly than would have been the case if the wool wash programme had been used. The order of the different compositions should not be affected by this procedure although the relative positioning may be changed by the amplification of damage resulting from increased agitation.

30 Example 2

Various wool fabrics were tested for weight loss due to repeated washing in either composition A(prior art) or composition B(the invention).

The fabrics were:

2.1 A lambs wool jumper

2.2 A botany wool jumper

2.3 A Shetland wool jumper

2.4 A wool/acrylic mixture jumper

Three 15cm square samples were cut from each article. One sample was kept for reference purposes and the other two were subjected to repeated washings in Compositions A and B. In each wash 100g of powder was administered by means of a shuttle. 1.5 kg of a 1:1:1 mix of cotton/terry/polycotton sheets were included in the wash as ballast. The water was 26°FH. Cloths were weighed before testing and then after 1, 5, 10 and 20 wash cycles. The results are given in Tables 2 to 5 which show the percentage weight losses for each material.

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<u>Table 2</u>

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LAMBSWOOL % Weight Loss				
	1 Wash	5 Washes	10 Washes	20 Washes
Composition A	5.6	16.0	45.3	66.7 @ 15 washes
Composition B	5.0	10.5	28.4	61.0

Table 3

5	BOTANY WOOL	% Weight Loss			
		1 Wash	5 Washes	10 Washes	20 Washes
10	Composition A	7.0	12.5	49.4	75.2 @ 16 washes
	Composition B	6.5	11.0	31.8	69.6

15 Table 4

	SHETLAND WOOL % Weight Loss				
20		1 Wash	5 Washes	10 Washes	20 Washes
	Composition A	6.5	9.6	24.7	64.1
25	Composition B	5.7	6.7	12.5	56.5

Table 5 30

	WOOL/ACRYLIC MIX % Weight Loss				
35		1 Wash	5 Washes	10 Washes	20 Washes
	Composition A	2.2	4.3	5.1	12.5
40	Composition B	2.1	3.5	5.9	10.6

It can be seen that the inclusion of the clay in Composition B reduces the weight loss. This is further demonstrated by Figures 1 to 3 which show the generally less damaged and holed cloths which have been washed in composition B as compared with Composition A.

Example 3

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To show that detergency is not being traded for reduced damage a series of detergency tests were carried out on standard test cloths. Reflectance measurements were made on the clothes before and after washing using an Ultrascan spectrophotometer. $\Delta R460*$ values were calculated and are tabulated in Table 7. It can be seen that the addition of the clay does not have an adverse effect on detergency even though the dilution caused by the addition results in a lower level of surfactant and enzyme in composition B.

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12.8

15.4

15.1

26.7

30.3

37.4

20.2

30.3

Composition B

		1000 million	_
5		م ،	30.3
10		ω	10.0
15		7	12.6
20		Q	13.2
25		<u>م</u>	26.4
30		4	30.1
35		3	37.4
40		5	21.8
		н 	28.7
45			Ā
50	لى لەر		Composition A
55	<u>Table 6</u>		Compo

Claims

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1. Use of from 2 to 30% by weight of a fabric softening clay as an additive to reduce or prevent wash damage of woollen articles in a fabric washing composition comprising an anionic surfactant, a nonionic surfactant and a proteolytic enzyme.

2. Use according to claim 1 wherein the clay is added in the form of a granule comprising 10 to 30% by weight nonionic surfactant.

3 Use according to claim 1 wherein the clay is selected from layered smectites and hectorites.

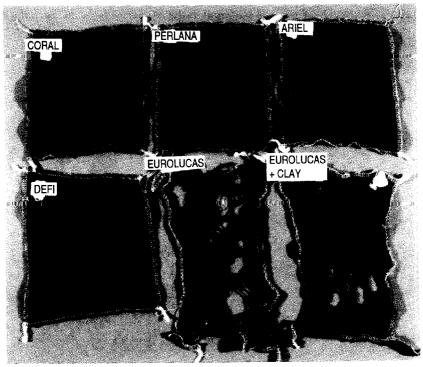
4 Use according to claim 1 wherein the clay is bentonite.

5. Use according to claim 1 wherein the composition further comprises Lipolytic enzyme.

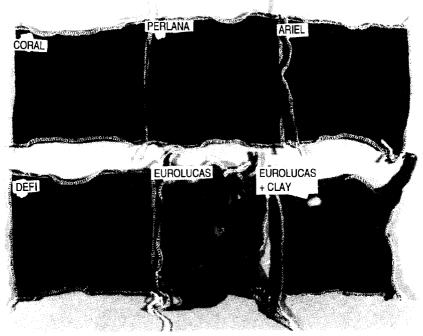
6. Use according to claim 1 wherein the pH of the composition in the wash is between 7.5 to 10.5, preferably 9 to 10.

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APPENDIX 13 - WOOL IMPOVERISHMENT.

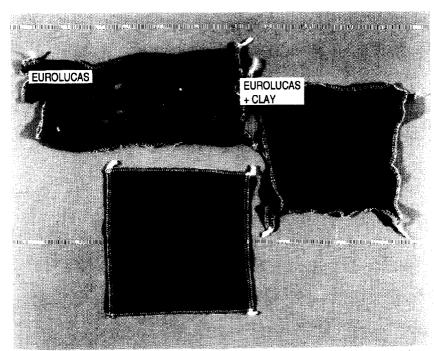


LAMBSWOOL AFTER 20 WASHES*.

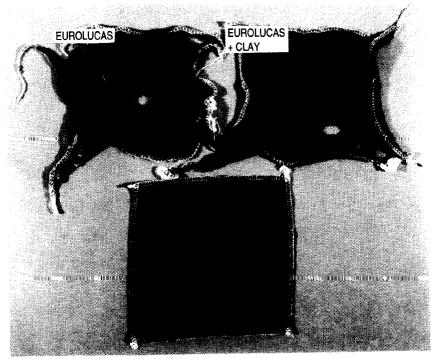


BOTANY WOOL AFTER 20 WASHES*.

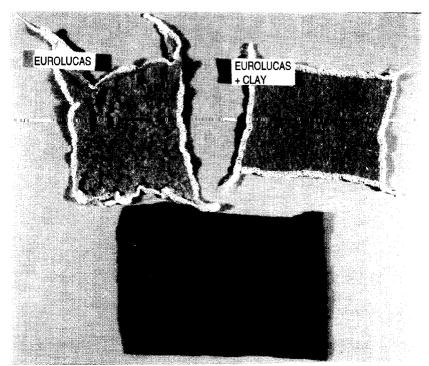
ONLY 15 AND 16 WASHES IN EURO - LUCAS POWER FOR LAMBSWOOL AND BOTANY WOOL RESPECTIVELY. APPENDIX 14 - WOOL IMPOVERISHMENT CONTD.



COMPARISON BETWEEN UNWASHED AND WASHED LAMBSWOOL (EURO - LUCAS x 15 CYCLES AND EURO - LUCAS + CLAY/NI GRANULES x 20 CYCLES)

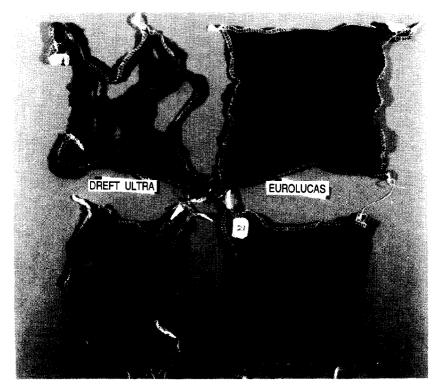


COMPARISON BETWEEN UNWASHED AND WASHED BOTANY WOOL (EURO - LUCAS x 16 CYCLES AND EURO - LUCAS + CLAY/NI GRANULES x 20 CYCLES).

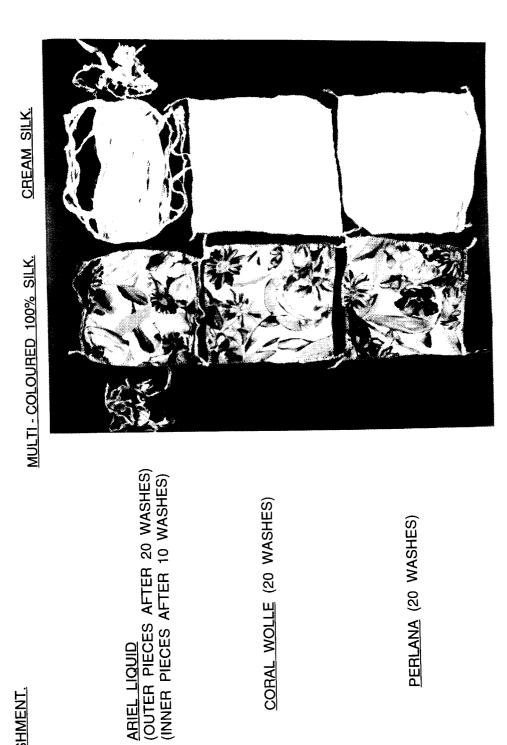


APPENDIX 15 - WOOL IMPOVERISHMENT CONTD.

<u>COMPARISON BETWEEN UNWASHED AND WASHED SHETLAND WOOL.</u> (EURO - LUCAS x 15 CYCLES AND EURO - LUCAS + CLAY/NI GRANULES x 20 CYCLES).



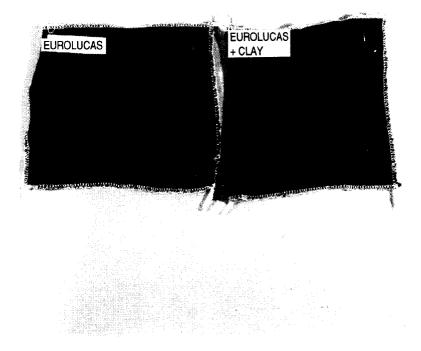
BOTANY AND LAMBSWOOL AFTER 10 WASH CYCLES IN EITHER EURO-LUCAS OR DREFT ULTRA.



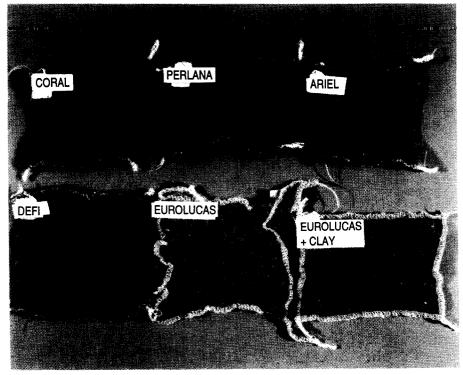
APPENDIX 16. SILK IMPOVERISI

SILK IMPOVERISHMENT.

APPENDIX 17 - PILLING.



AN ILLUSTRATION OF THE REDUCTION IN WOOL PILLING FOR INCLUSION OF CLAY/NI GRANULES IN EURO - LUCAS POWDER.



APPENDIX 18 - DYE LOSS AND TRANSFER

DYE LOSS WITH EURO - LUCAS POWDER (PHOTOGRAPH ALSO ILLUSTRATES REDUCTION IN WOOL DAMAGE FOR CLAY IN EURO - LUCAS)

DYE TRANSFER WITH EURO - LUCAS

