

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 614 966 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
23.12.1998 Bulletin 1998/52

(51) Int Cl.⁶: **C11D 3/12, C11D 3/386,
C11D 1/83**

(21) Application number: **94300871.4**

(22) Date of filing: **07.02.1994**

(54) **Use of a fabric softening clay**

Verwendung eines Gewebe weichmachenden Tonmaterials

Utilisation d'une argile comme assouplissant de tissus

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

(30) Priority: **10.03.1993 GB 9304898**

(43) Date of publication of application:
14.09.1994 Bulletin 1994/37

(73) Proprietors:
• **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
GB

• **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
CH DE ES FR IT LI NL SE

(72) Inventors:
• **Bishop, David Paul, Unilever Research Port
Wirral, Merseyside, L63 3JW (GB)**

• **Prescott, Andrew John**
Wirral, Merseyside, L63 3AN (GB)

(74) Representative: **Fransella, Mary Evelyn et al**
Unilever PLC
Patent Division
Colworth House
Sharnbrook
Bedford MK44 1LQ (GB)

(56) References cited:
EP-A- 0 277 571 **EP-A- 0 612 841**
DE-A- 2 162 177 **FR-A- 2 247 530**
GB-A- 1 367 477

• **DATABASE WPI Week 9131 Derwent**
Publications Ltd., London, GB; AN 91-228529 &
SU-A-1 606 557 (KUTAISK POLY), 15 November
1990

EP 0 614 966 B1

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

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-A-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 with a detergent active material. Enzymes are suggested as a possible additive to the composition.

EP-A-612 841, published on 31.08.94, is a copending application which discloses compositions comprising a clay to control/prevent pilling of fabrics made of keratin containing fibres whilst providing a softening benefit.

DE-A-2162177 discloses washing compositions comprising a proteolytic enzyme and an anionic surfactant including soap. EP-A-0-277 571 discloses washing compositions comprising low levels of protease enzymes, anionic surfactants and nonionic surfactant, used in combinations with clay softeners for the washing of woollen fabrics.

Likewise SU-A01606557 discloses detergent compositions comprising proteolytic enzymes and bentonite for washing woollen fabrics.

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 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 other than pilling 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 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 (trademark) clay from Greece, GELWHITE (trademark) from Texas USA, Willemse from South Africa and VOLCLAY BC (trademark) 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 a 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 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 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 (C₈-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 sulphonates and sodium (C₁₆-C₁₈) alkyl sulphates.

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 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 (C₈-C₁₈) 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 so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

5 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.

10 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.

15 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.

20 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.

25 Proteolytic enzymes that may be used in the present invention include the Savinases, such as Savinase 6.0T ((trademark) ex Novo), Opticlean ((trademark) Solvay) and Maxacal (trademark), (Ibis) also Alcalases such as Alcalase 2.34 LVX and Esperase 8.0 (both trademarks), Novo), Optimase (trademark, Solvay) and Maxatase (trademark, Ibis). Lipases and cellulases may also be included in the composition.

30 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 cationic 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 trichlorisocyanuric 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.

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

40 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;

45 Figure 3 is a photograph of a comparison between unwashed and washed Lambswool cloths washed in compositions with and without clay;

Figure 4 is a photograph of a comparison between unwashed and washed Botany wool cloths washed in compositions with and without clay;

50 Figure 5 is a photograph of a comparison between unwashed and washed Shetland wool cloths washed in compositions with and without clay;

Figure 6 is a photograph of Botany wool and Lambswool cloths washed in compositions without clay; and

55 Figure 7 is a photograph of wool cloths washed in a composition without clay (Euro-Lucas) and illustrates the effect of clay upon wool damage; also dye loss with Euro-Lucas powder is illustrated.

EP 0 614 966 B1

Example 1

Fabric washing powders of the following compositions were prepared by conventional techniques. The clay non-ionic 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.

Table 1

	Composition A	Composition B
Anionic	18.5	16.65
Nonionic	4.6	4.14
Savinase 6.0T	0.65	0.85
Zeolite	35.9	32.31
Sodium carbonate	12.4	11.16
Polymer	4.4	3.96
Sodium bicarbonate	4.0	3.6
Water	14.5	13.05
Lipolase 100T	0.30	0.27
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.

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.

Table 2

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

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

Table 4

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

Table 5

WOOL/ACRYLIC MIX	% Weight Loss			
	1 Wash	5 Washes	10 Washes	20 Washes
Composition A	2.2	4.3	5.1	12.5
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

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. ΔR_{460}^* 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.

5
10
15
20
25
30
35
40
45
50
55

Table 6

	1	2	3	4	5	6	7	8	9
Composition A	28.7	21.8	37.4	30.1	26.4	13.2	12.6	10.0	30.3
Composition B	30.3	20.2	37.4	30.3	26.7	15.1	15.4	12.8	30.6

Claims

- 5 1. Use of from 2 to 30% by weight of a fabric softening clay as an additive to reduce or prevent wash damage other than pilling of woollen articles in a fabric washing composition comprising an anionic surfactant, a nonionic surfactant and a proteolytic enzyme.
- 10 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.
- 15 5. Use according to claim 1 wherein the composition further comprises a 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.

Patentansprüche

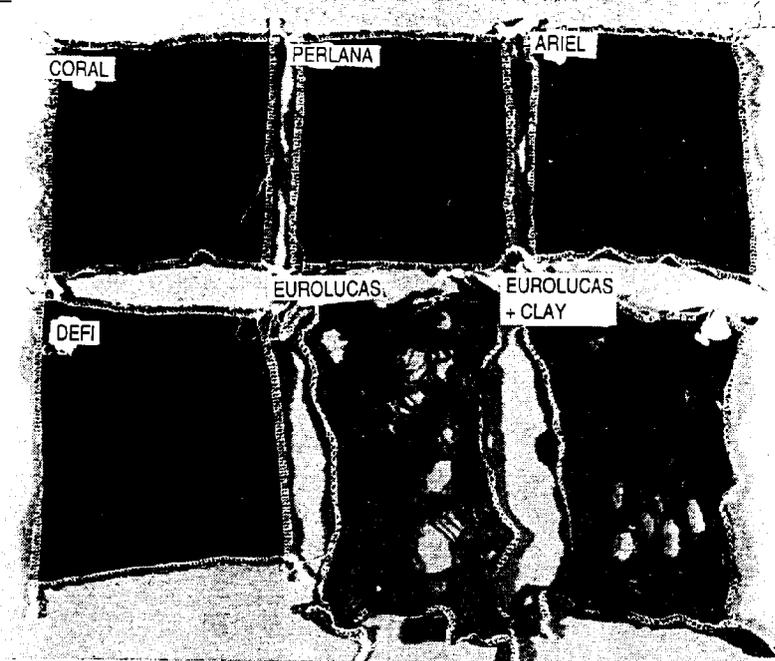
- 20 1. Verwendung von 2 bis 30 Gewichtsprozent eines Textil weichmachenden Tons in einem ein anionisches Tensid, ein nichtionisches Tensid und ein proteolytisches Enzym umfassenden Textilwaschmittel als Additiv zur Vermin-
derung oder zur Verhinderung einer Schädigung, außer Pillbildung, von wollenen Gegenständen durch Waschen.
- 25 2. Verwendung nach Anspruch 1, wobei der Ton in Form eines Granulats, umfassend 10 bis 30 Gewichtsprozent nichtionisches Tensid, zugegeben wird.
3. Verwendung nach Anspruch 1, wobei der Ton ausgewählt ist aus Schicht-Smectiten und -Hectoriten.
- 30 4. Verwendung nach Anspruch 1, wobei der Ton Bentonit ist.
5. Verwendung nach Anspruch 1, wobei das Mittel weiterhin ein lipolytisches Enzym umfaßt.
- 35 6. Verwendung nach Anspruch 1, wobei der pH-Wert des Mittels in der Waschlauge zwischen 7,5 bis 10,5, vorzugsweise 9 bis 10, liegt.

Revendications

- 40 1. Utilisation de 2 à 30% en poids d'une argile d'assouplissement des textiles comme additif pour réduire ou empêcher l'endommagement par le lavage autre que le peluchage des articles en laine dans une composition de lavage des
tissus comprenant un tensioactif anionique, un tensioactif non ionique et une enzyme protéolytique.
- 45 2. Utilisation selon la revendication 1, dans laquelle on ajoute l'argile sous forme d'un granule comprenant 10 à 30% en poids de tensioactif non ionique.
3. Utilisation selon la revendication 1, dans laquelle on choisit l'argile parmi les smectites et les hectorites stratifiées.
- 50 4. Utilisation selon la revendication 1, dans laquelle l'argile est la bentonite.
5. Utilisation selon la revendication 1, dans laquelle la composition comprend de plus une enzyme lipolytique.
- 55 6. Utilisation selon la revendication 1, dans laquelle le pH de la composition dans le lavage est entre 7,5 et 10,5, de préférence 9 et 10.

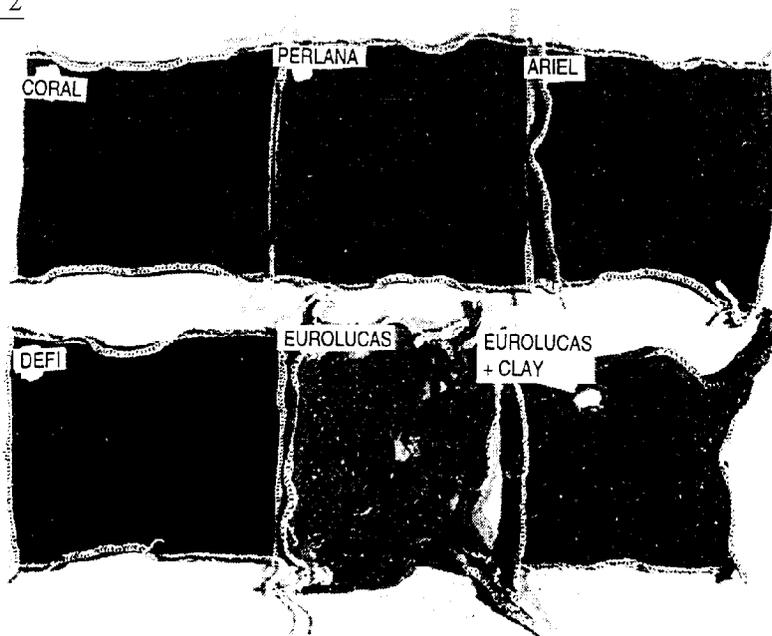
WOOL IMPOVERISHMENT.

Figure 1



LAMBSWOOL AFTER 20 WASHES*.

Figure 2

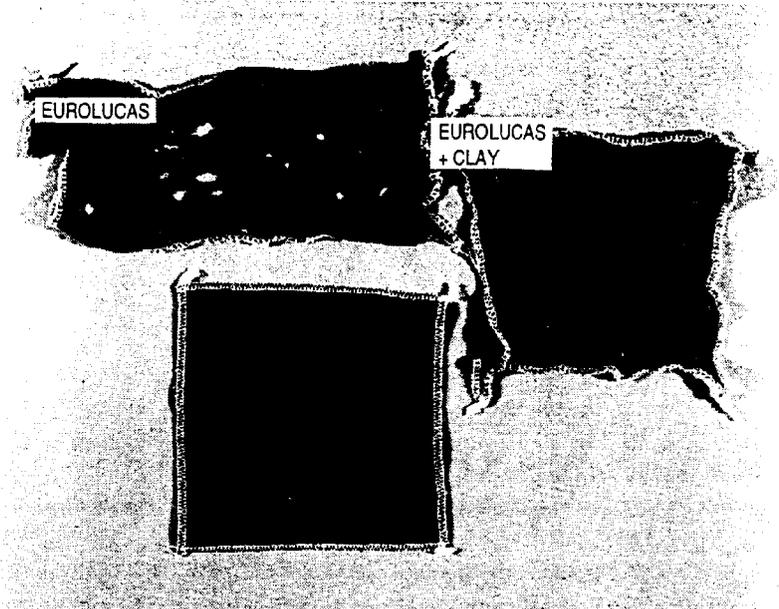


BOTANY WOOL AFTER 20 WASHES*.

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

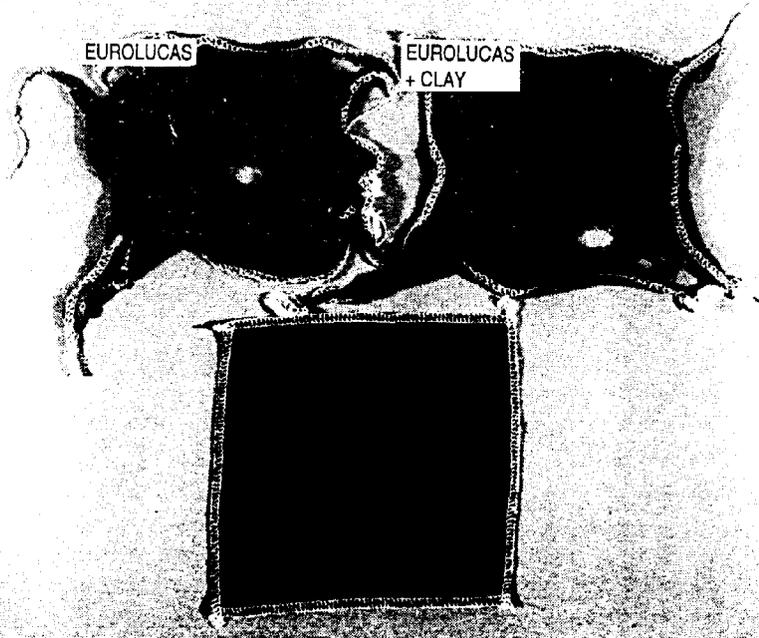
WOOL IMPOVERISHMENT CONTD.

Figure 3



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

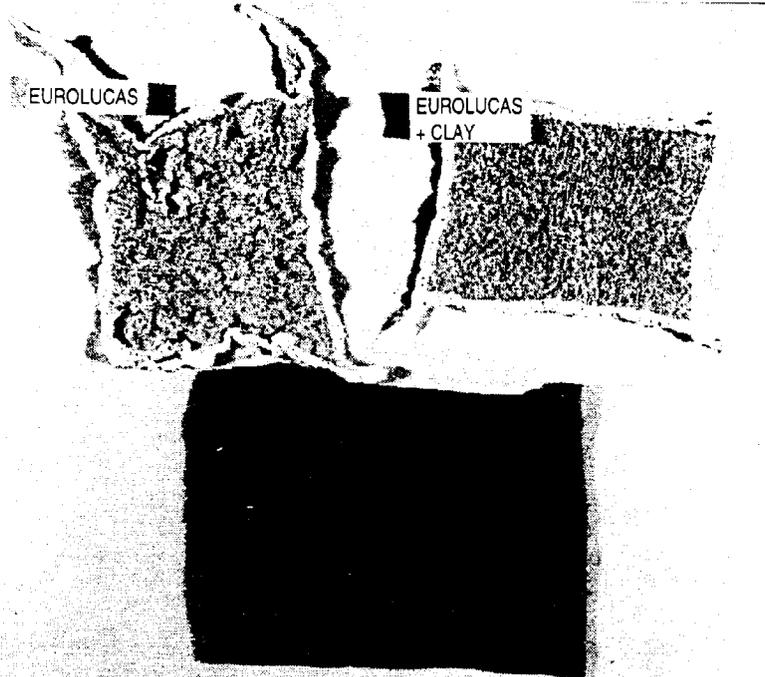
Figure 4



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

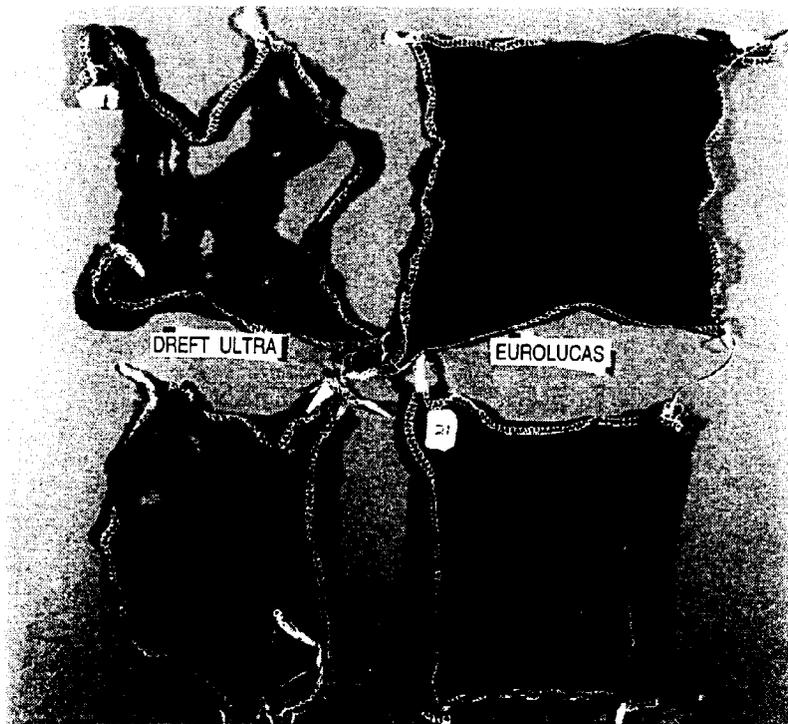
WOOL IMPOVERISHMENT CONTD.

Figure 5



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

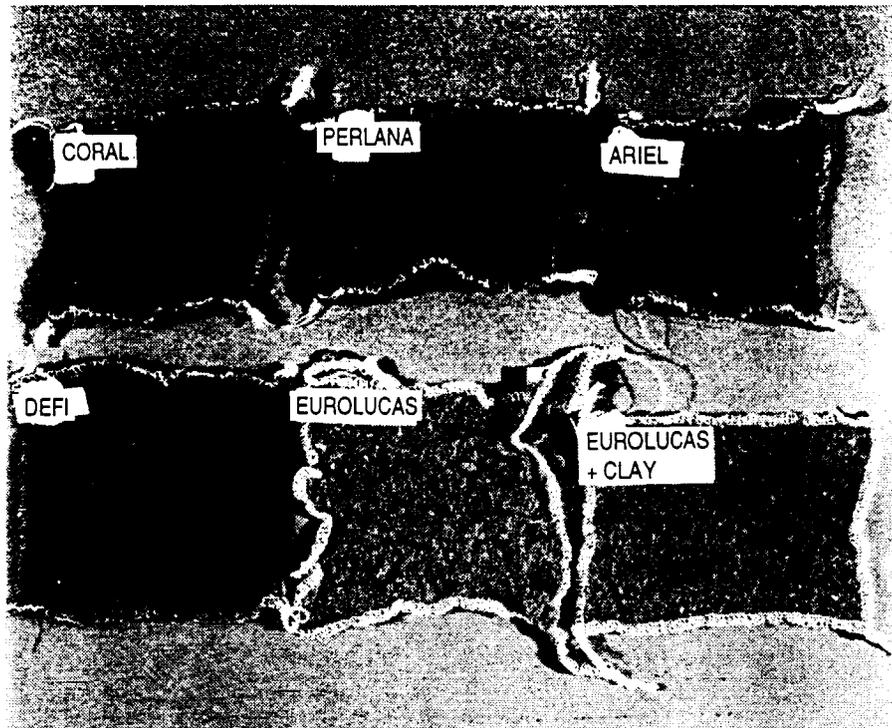
Figure 6



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

DYE LOSS AND TRANSFER

Figure 7



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