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Investigation of the Conditioning Effect of Collide HQS on Fabrics

Keywords: Proteins, conditioning agents, fabric care

1 . Introduction

Proteins are commonly used in the textile industry in specialist niche applications. Industry examples include their use as sacrificial proteins in the fine/ small diameter wool-dyeing process, repairing agents for chemically damaged wool, setting agents, bulking agents for woollen fabrics/carpets, and as aids for even-penetration of dyes into a range of fibres. They also find use in consumer markets such as fabric conditioners/softeners and detergents targeting both natural fibres like cotton, silk, and wool, as well as synthetics. In fabric care products proteins provide functional points of difference and label claims; evocative protein derivatives such as silk and cashmere have been particularly successful.

2. Background

Croda has been at the forefront of protein technology for the cosmetic industry for over 20 years, and it is this technology that has been successfully transferred to the textile auxiliary and consumer product industries. In cosmetics, proteins are used to impart a wide range of functional benefits such as:

- Moisture binding & conditioning
- Film-forming
- High substantivity
- Viscosity & texture modification
- Emulsion & foam stabilisation

A broad range of proteins, amino acids and their derivatives (for example quaternised proteins) have been developed to provide conditioning effects for both skin and hair care applications. The versatility of these products provide opportunities for cosmetic manufacturers to make claims such as skin moisturisation and smoothing, as well as hair care benefits including conditioning, softening, volumising, shine enhancing, and fibre strengthening. The mechanism for protein functionality has been explained by their ability to penetrate, and be substantive to, the skin and hair fibres. As the cuticle structure of hair fibre is very similar to wool fibre, it was a natural step to apply Croda's extensive protein technology to fabric conditioners/softeners and detergents, where hydrolysed proteins and/or their derivatives have been evaluated as repairing and conditioning agents for natural textiles such as wool, cotton, cashmere, mohair, and even synthetics such as nylon. Proteins and derivatives are known to impart a number of consumer-perceptible functional benefits to modern fabrics:

- Conditioning
- Softening
- Anti-static
- Anti-pilling
- Extended fibre life

Proteins can be added to fabric care products at low inclusion levels (0.04 % -0.20% active). Even at such low addition levels differences in fabric handle can be readily detected in panel evaluations. The proteins that show the greatest conditioning effect as demonstrated via panel testing are the alkyl quaternary derivatives. The chemistries include:

- Coltide HQS
  Stearyldimonium hydroxypropyl hydrolysed wheat protein
- Coltide BQS
  Stearyldimonium hydroxypropyl hydrolysed cotton protein
- Coltide SQM
  Cocodimonium hydroxypropyl hydrolysed silk protein
- ColtideWQM
  Cocodimonium hydroxypropyl hydrolysed wool protein
- Coltide CQS
  Stearyldimonium hydroxypropyl hydrolysed collagen protein

As the alkyl quaternary derivatives had proved successful in panel tests, it was decided that further work to produce quantitative data should be undertaken. Coltide HQS was selected as the first test alkyl quaternary derivative to be evaluated with cotton and wool as the test fabrics. In order to quantify the conditioning benefits of Coltide HQS it was incorporated into a standard fabric conditioner/softener so that a scientific study could be conducted by an independent textile testing house. The washed fabrics were evaluated using the following methods:

1 . Subjective Handle Tests

2. Protein Deposition

Measurements

3. Scanning Electron Microscopy

4. Dynamic Mechanical Thermal Analysis

5. Wettability Tests

The results showed a significant improvement in fabric conditioning, i.e., improved lubricity and reduction in fibre erosion, and supported the results obtained from the previous panel evaluations.

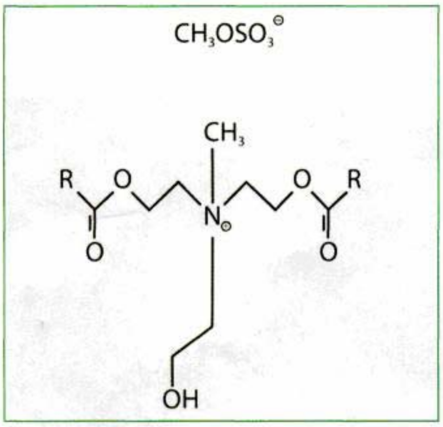
3. Conditioning agents used

3.1 Coltide HQS

Coltide HQS is a C18 alkyl quaternary wheat protein derivative (Stearyldimonium hydroxypropyl hydrolysed wheat protein). The cationic quaternary group is covalently attached to the protein via an addition reaction to the side chain amino groups **(Fig. 1).** Over 70% of the available amino groups on the protein have been substituted and this results in the protein becoming highly cationic (isoionic point pH >10).

3.2 Fabric Softener

The base fabric softener to which the Coltide HQS was added was a 5 % solution of di-(tallow carboxyethyl) hy-droxyethyl



methylammonium metho-sulphate; an esterquat **(Fig. 2).**

Fig. 2 Di-(tallowcarboxyethyl) hydroxy-ethyl methylammonium methosulphate

4. Fabrics used

The fabrics evaluated in the study were:

1 . 100 % cotton terry towelling - 500 g/sq. m
2. 100% cotton yarn
3. 100% wool - machine washable Hercosett treated-380 g/sq. m
4. 75/25 wool/nylon yarn - machine washable.

5. Machine washing protocol

The cotton and wool fabrics were washed in a domestic (Miele) washing machine using the following cycle:

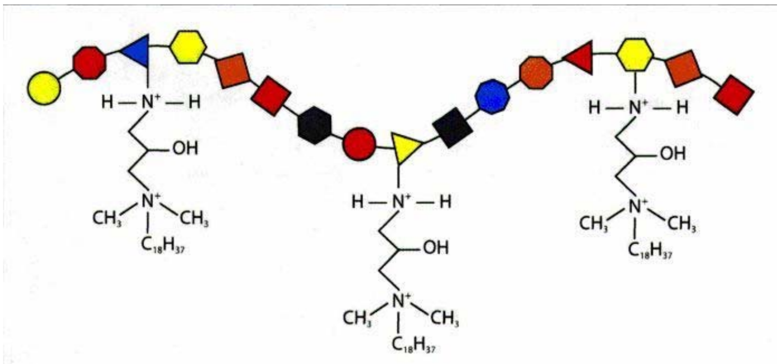


Fig. 1 Structure of Coltide HQS

Detergent wash -> Spin -> Rinse -> Spin -> Rinse -> Spin -> Rinse -> Spin -> Conditioner rinse -> Spin

The quantities of materials used were:

Fabric load	2 kg
Detergent wash	Containing standard ECE detergent (100 g per load) and sodium perborate (15 g per load). 12 litres of wash liquors.
Wash temperature	40 °C.
Rinse 1	7.0 litres of rinse liquors.
Rinse 2	7.0 litres of rinse liquors.
Rinse 3	7.0 litres of rinse liquors.
Conditioner rinse	Containing 90 mis of the test or control conditioner per load. 6.5 litres of conditioner rinse liquors.
Water hardness	0.040 mg CaCO3/litre

The fabrics were line dried after each wash cycle and a total of 20 wash cycles were used. Fabric tests were carried out after 10 and 20 wash cycles.

6. Conditioner formulations

Conditioner (Control)

5.0% esterquat (see section 3).

Conditioner (Test)

5.0% esterquat + 0.5% Coltide HQS

0.5% Coltide HQS is equivalent to - 0.1 % on an actives basis.

For the purpose of this paper, fabrics treated with the control conditioner have been termed control fabrics, those treated with the test conditioner have been termed test fabrics. Unwashed fabrics have been termed untreated fabrics.

7. Results

7.1 Subjective Handle Tests

There are two main reasons for using a fabric softener:

1 . It imparts increased 'body[1] (a bulking out effect) to the fabric.
2. It makes the fabric feel softer, usually as a consequence of an increase in body, and/or a reduction in fibre erosion and/or an increased lubricating effect.

These are the effects that the consumer can instantly perceive and as such are very important when marketing fabric conditioners. Additives that can significantly improve the effectiveness of a conditioner in terms of fabric softness, such that it is perceptible by the consumer, will have an immediate commercial advantage over ordinary conditioners. A point of difference due to innovation will also be recognised.

Subjective handle tests were carried out on cotton terry towelling and wool after 10 and 20 wash cycles. Twenty assessors (10 male and 10 female) were used for the tests and each assessor was asked to evaluate the test and control fabrics and report a result as either a 'Preference[1] for one or the other or 'No Preference[1] for either. The results for wool as shown in Fig. 3 indicate that although the test fabric is preferred after 10 and 20 wash cycles, one could not argue that the differences are statistically significant. A reason for this is that the wool chosen for this study was pre-treated with Hercosett resin to make it machine washable. As a result it was more difficult to make subjective handle assessments. Also, the desired 'handle' for wool is different from that of cotton and hence the interpretation of subjective handle becomes even more difficult.

The results for cotton terry towelling as shown in Fig. 4 indicate that the test fabric is preferred after 10 and 20 wash cycles. The results, using student t-test statistical analysis, are significant after 10 wash cycles ($t = 3.58$; significance at the 0.5 % level) and conclusive after 20 wash cycles.

The results for cotton terry towelling show that the perceptible differences in 'handle' between the test and control fabrics increases with the number of wash cycles. There are two possible explanations for this observation:

1. That Coltide HQS is 'building-up' on the cotton, with successive wash cycles, and thus provides an increasing lubricating effect that gives rise to continued improvement in 'handle'.

However as described below, although some deposition of Coltide HQS will occur and thus give rise to lubricity, continued 'build-up' on the cotton does not occur. This is backed up by the wet-tability results

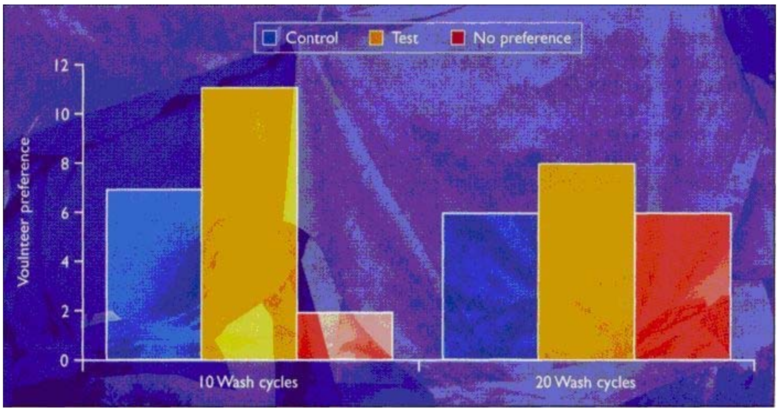


Fig. 3 Subjective handle results on wool

that show that the wetting characteristics of the fabric remain almost intact. This would not be the case if 'build-up' occurred. The second explanation is more probable.

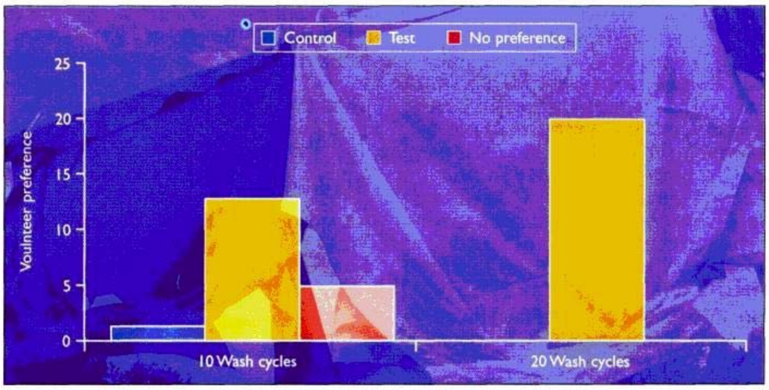


Fig. 4 Subjective handle results on cotton

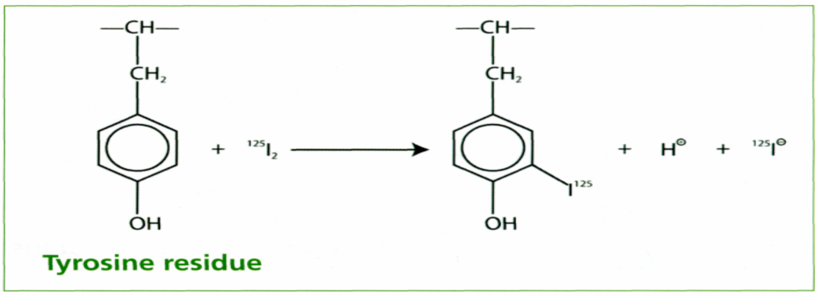


Fig. 5 Iodination of tyrosine residues in Coltide HQS

2. That Coltide HQS helps to reduce the deterioration of the fabric which occurs as a consequence of repeated washing. Retention of the original physical characteristics of the cotton result in a better 'handle/

7.2 Protein Deposition Measurements

The amount of Coltide HQS deposited on the cotton or wool fibres can be de termined using an Iodine-125 radiola-belling technique. This technique involves covalently 'tagging[1] the tyro-sine residues of the protein with radioactive Iodine-125 **(Fig. 5)** and measuring the radioactivity on the substrate after treatment.

Radio-labelled Coltide HQS was added to the conditioner, as per test formulation, and the machine wash protocol was adopted for the treatments. Cotton terry towelling and wool fabrics were given 5 wash cycles and radioactivity counts were measured after the 1^{st}, 3^{rd} and 5^{th} wash. The level of active Coltide HQS in each conditioner rinse was equivalent to 0.0014 %. (The deposition curve shows the error bars for a data spread of 2 standard deviations). The results for wool **(Fig. 6)** show that Coltide HQS is deposited on the fibres and that after 5 wash cycles the uptake begins to plateau at approximately 0.002% deposition. Each of the wool fabrics, after 1, 3 and 5 treatments, was then washed once with detergent and rinsed 3 times with water, and the radio-activity was again measured to determine how much of the Coltide HQS remained on the wool. This is termed the protein 'Sub-stantivity'[1] and the results are shown in Fig. 7.

The substantivity begins to plateau after 5 wash cycles and is lower than one might expect. The reason for the low substantivity can be attributed to three factors, i.e., the level of active Coltide HQS in the conditioner is low, the fabric has been washed with a detergent and then rinsed, and the Hercosett resin on the wool surface has reduced the level of substantivity of Coltide HQS.

For cotton (Fig. 8) a similar deposition effect was shown but the plateau begins after 3 wash cycles at approximately 0.007%.

The substantivity results (Fig. 9) differ from those for wool in that the plateau does not occur after 5 wash cycles.

From these results we can conclude that:

1.Coltide HQS is deposited on the wool and cotton fabric.

2.There is no build-up of Coltide HQS on wool or cotton.

3.That, for cotton in particular, an increasing amount of the deposited protein remains substantive after repeated wash cycles, i.e., less of the deposited protein is washed off during the detergent and rinse cycles.

It is therefore possible that the substantive Coltide HQS may provide sufficient lubrication to reduce fibre damage, resulting from physical abrasion, during the machine wash cycles.

7.3 Scanning Electron Microscopy (SEM)

This technique was used to determine whether any physical changes on the surface of the cotton fibre could be observed. Micrographs were taken after 10 and 20 wash cycles, for both the control and test fibres, to evaluate the extent of fibrillation on the fibre surface. All micrographs were taken atx1800 magnification. A large number of micrographs were taken of each type of fibre and the ones shown in this report represent an average overview.

Cotton

Fig. 10 shows the SEMs for the untreated and control fibres after 10 and 20 wash cycles. It can be seen that there is some fibrillation of the fibre after 10 wash cycles but significantly more after 20 wash cycles. The test fibres in **Fig. 11** show that there is almost no fibrillation after 10 wash cycles, however some is observed after 20 wash cycles. It can be clearly seen from **Figs. 10** and 11 that there is significantly more fibrillation on the control fibres, particularly after 20 wash cycles.

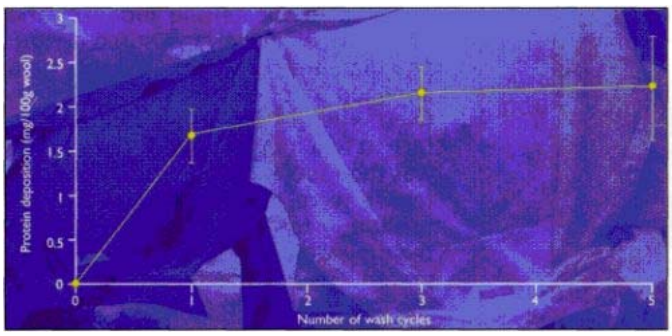


Fig. 6 Deposition of Coltide HQS on wool

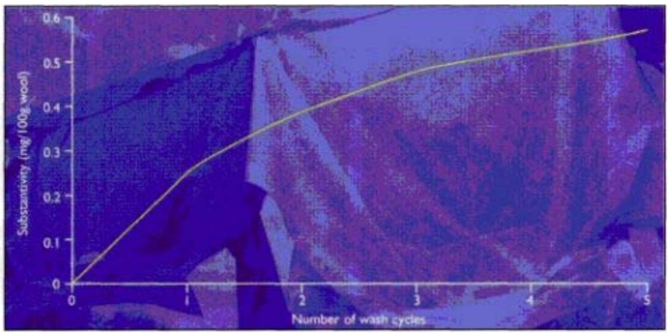


Fig. 7 Coltide HQS substantivity to wool

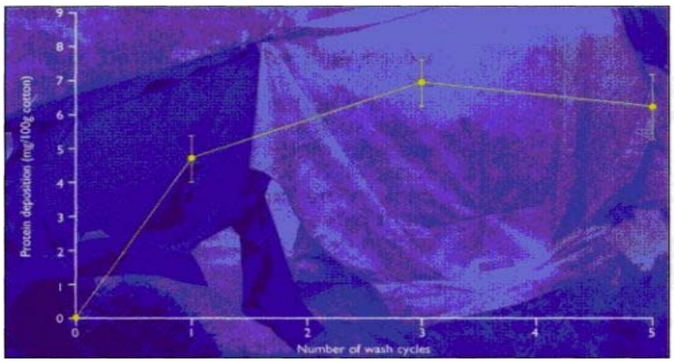


Fig. 8 Deposition of Coltide HQS on cotton

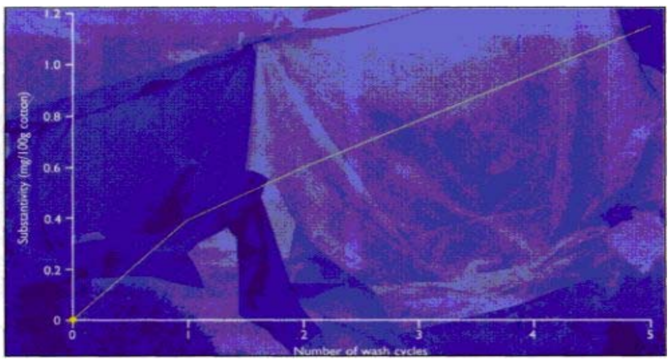


Fig. 9 Coltide HQS substantivity to cotton

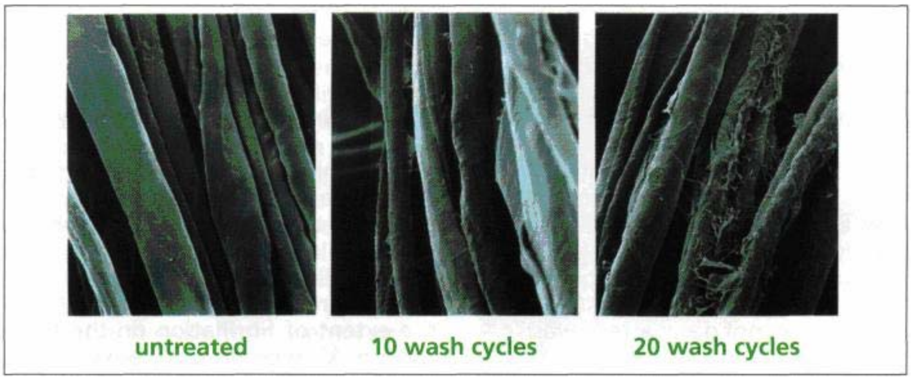


Fig. 10 SEMs of untreated and control fibres after 10 and 20 wash cycles

Fig. 11 SEMs of untreated and cotton test fibres after 10 and 20 wash cycles

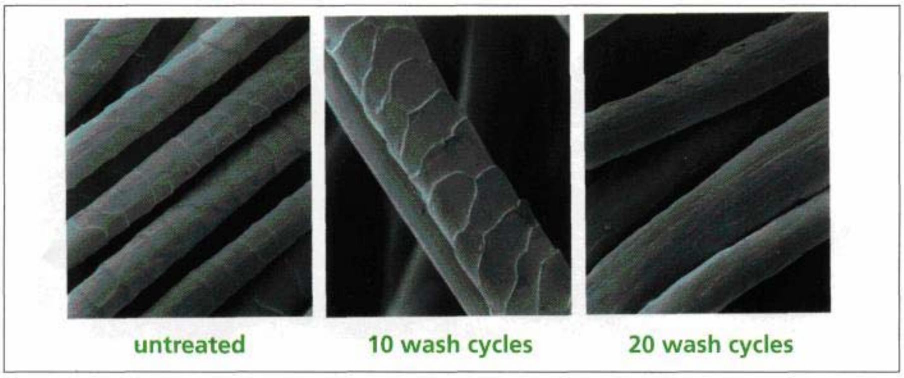


Fig. 12 SEMs of untreated and wool control fibres after 10 and 20 wash cycles

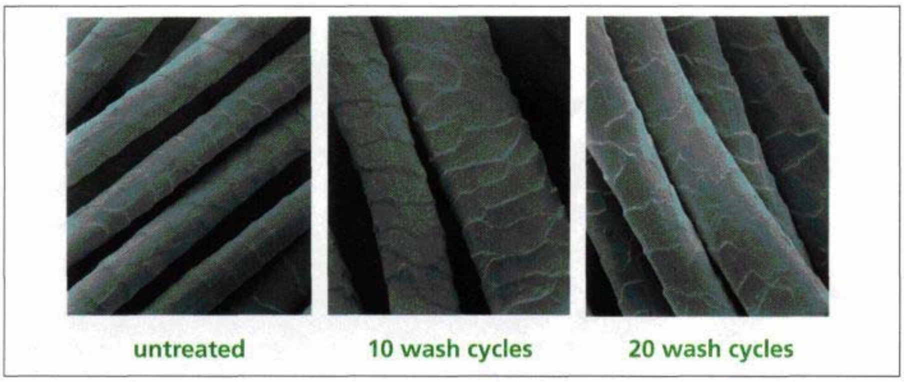


Fig. 13 SEMs of untreated and wool test fibres after 10 and 20 wash cycles

Wool

Fig. 12 shows the SEMs for the untreated and control fibres after 10 and 20 wash cycles. It can be seen that after 10 wash cycles the integrity of the fibre is maintained, but after 20 wash cycles a large proportion of the cuticle has been stripped off. The test fibre **(Fig. 13)** also looks very similar to the untreated fabric after 10 washes and after 20 washes some of the cuticle has been compromised but not nearly as much as that of the control fibres.The overall conclusion from the SEM study is that Coltide HQS is preventing erosion of both the cotton and wool fibres.

7.4 Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is a thermal analysis tool which gives a representation of the molecular transitions and displacements in a polymer/fibre when subjected to an applied sinusoidal force over a specified temperature range. In this study the DMTA was used to provide information on molecular changes within the fibre and changes in fibre displacement due to surface lubricity. The mechanics of the system are somewhat complicated but, put as simply as possible, the sample fibres were analysed in the tensile mode of the DMTA. An accurately measured (length and diameter) piece of yarn was held between two clamps; one clamp is fixed whereas the other clamp is attached to a moveable rod. The sample was then subjected to a small constant tensile force of 0.1 N, followed by an oscillating force of frequency 1Hz via the moveable rod. A furnace was then placed around the tensile head and the temperature lowered to -50°C before being slowly raised at 4 °C/min. up to200°C.

Displacement and Tan 6 curves were generated. The Tan 8 curve is a measure of the ratio of the energy lost (dissipated as heat) per cycle to energy stored (and hence recovered) during an applied sinusoidal force. It determines whether any phase transitions occur, such as glass transitions, softening and melting and crystallinity effects; all of which are indicated by a peak in the Tan 6 curve. The displacement curve simply measures any elongation or contraction of the sample.

Cotton

Fig. 14 shows the Tan 8 curve for cotton after 10 wash cycles. It can be seen that there is very little difference between

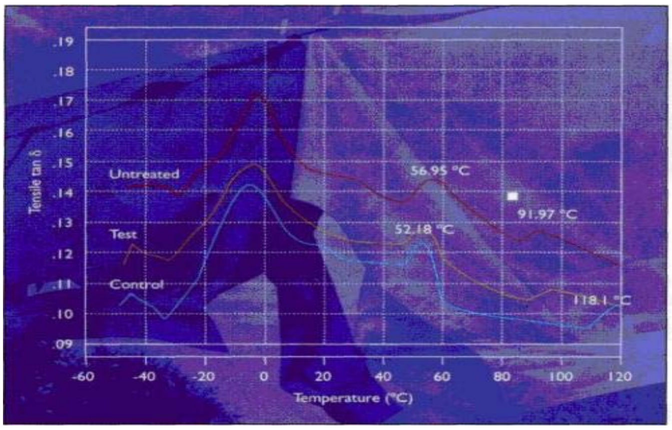


Fig. 14 Tan 5 curve for cotton after 10 washes

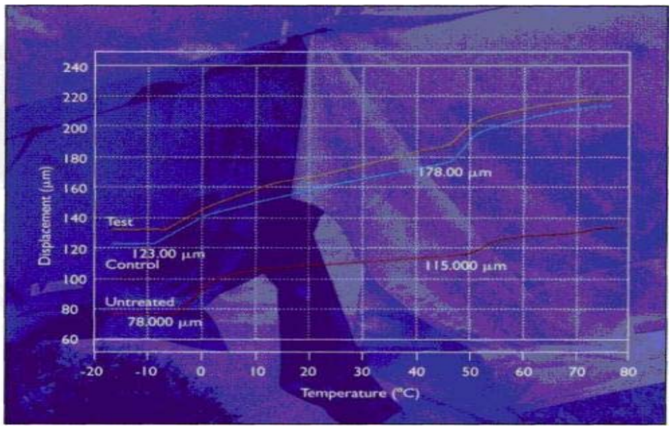


Fig. 15 Displacement curve for cotton after 10 washes

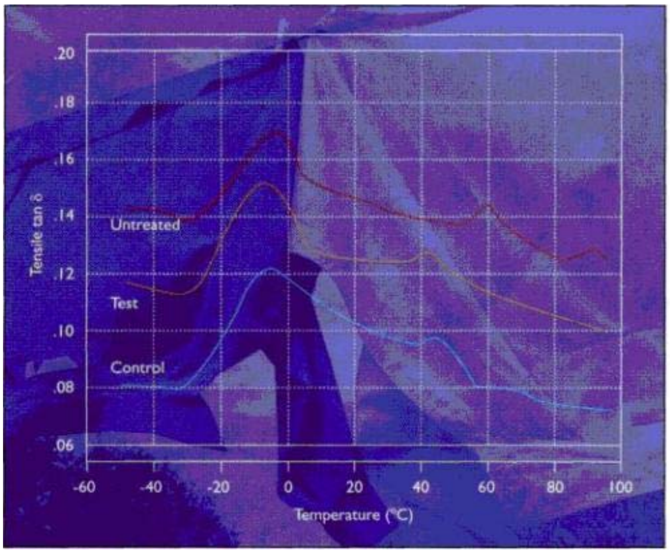


Fig. 16 Tan 5 curve for cotton after 20 washes

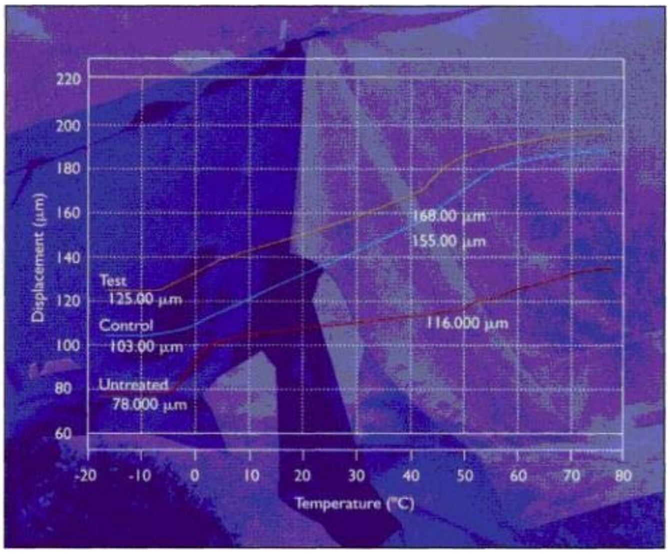


Fig. 17 Displacement curve for cotton after 20 washes

the untreated, test and control samples. The displacement curve **(Fig. 15)** shows that a lubricating effect has taken place for both the test and control samples compared to the untreated sample, but there is no significant difference between the test and control samples.

The same conclusions were applicable after 20 wash cycles as shown in **Fig. 16** and **Fig. 17** respectively.

Wool

The results for wool, however, did show significant differences between the test and control samples. Fig. 18 shows the Tan 6 curve after 10 wash cycles and it can be seen that the test sample curve is very similar to that of the untreated sample. The control sample, however, is different indicating that phase transitions have taken place. The displacement curve **(Fig. 19)** also indicates significant differences between the test and control samples. The test sample showed the largest displacement, particularly between 10°C and 40 °C, indicating most improved fibre lubricity. The observed change in displacement, for the test sample, is purely as a result of improved lubricity because there are no phase transition differences between the untreated and test samples as shown by the Tan δ curves. The Tan 8 curve **(Fig. 20)** of the test sample after 20 wash cycles was very similar to that after 10 wash cycles. The Tan 8 curve for the control sample after 20 wash cycles was distinctly different from that after 10 wash cycles. The large peak observed at -10°C to 50°C indicates molecular degradation of the fabric. The displacement curve **(Fig. 21)** for the test sample, after 20 wash cycles, is again similar to that after 10 washes, with the sample stretching over the temperature range -20 °C to 40 °C and then resuming the pattern of the untreated sample. This again is

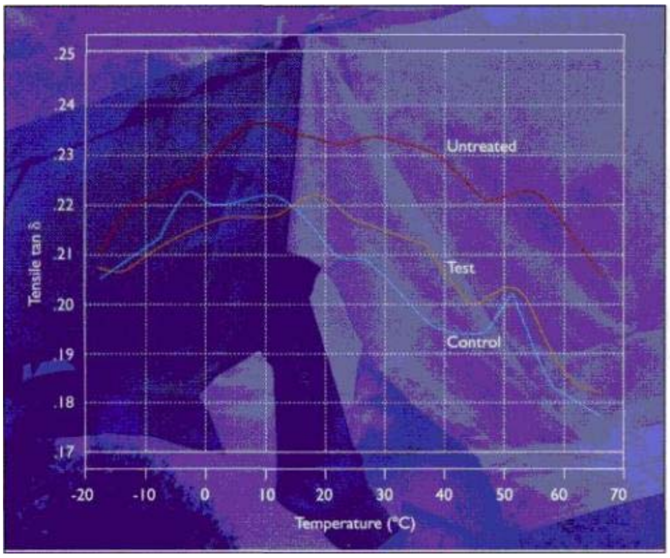


Fig. 18 Tan 5 curve for wool after 10 washes

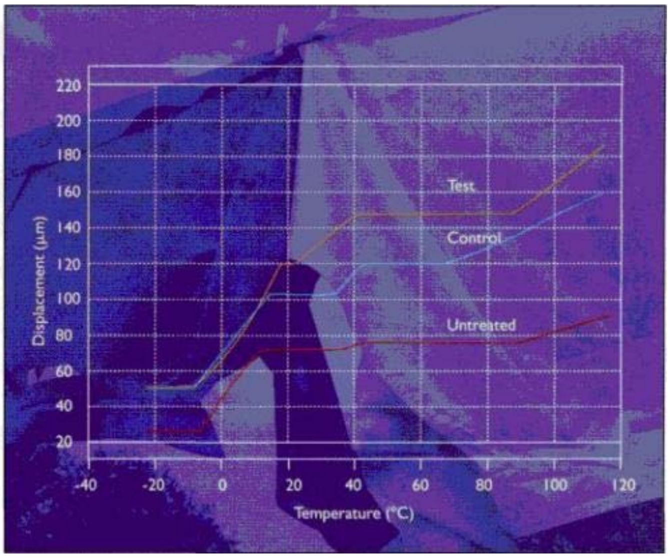


Fig. 19 Displacement curve for wool after 10 washes

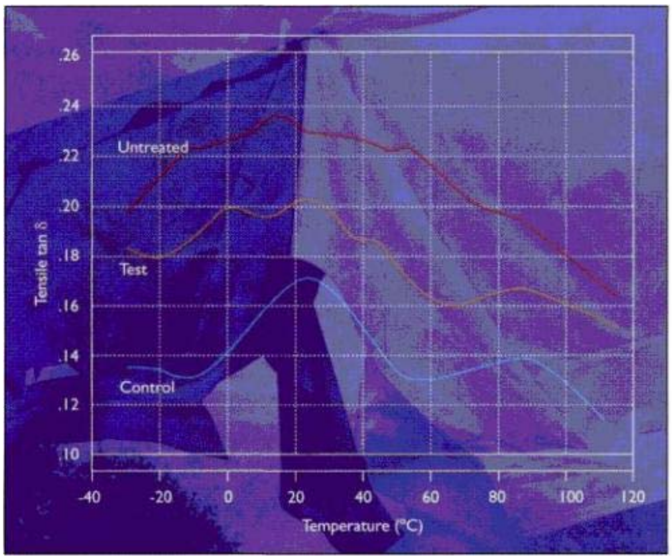


Fig. 20 Tan 5 curve for wool after 20 washes

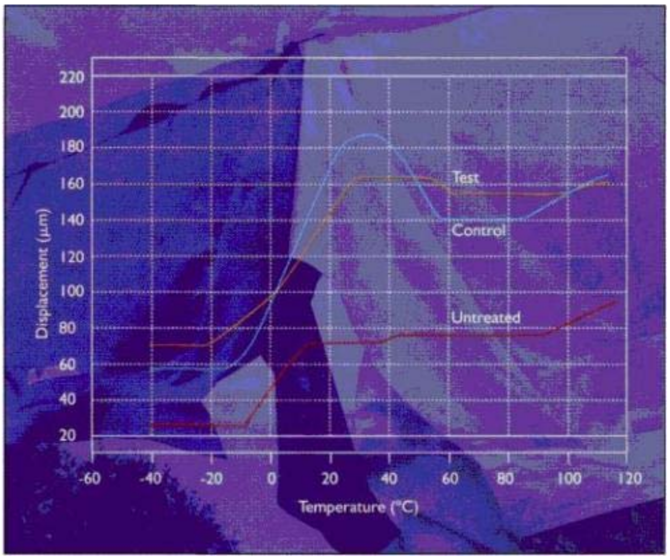


Fig. 21 Displacement curve for wool after 20 washes

predominantly as a result of increased fibre lubrication. The displacement curve for the control sample, after 20 wash cycles, differed significantly from that after 10 wash cycles in that the sample stretched quite substantially over the temperature range -20 °C to 30 °C. Although one may be led to conclude that this is also due to increased lubricity, this is in fact not the case. There is some displacement caused by improved lubricity but most of the displacement change is a result of degradative weakening of the sample as reflected in the Tan 5 curve at this temperature range. This is backed up by the contraction that is observed in the sample between 35 °C to 60 °C. Contraction is normally as a result of re-orientation of degraded polymer chains which produces a temporary recovery in strength of the sample. In conclusion, the DMTA study has shown that differences in phase transitions or displacement between test and control samples were not detected for cotton after 10 or 20 wash cycles. Whether this is due to the nature of the polymer structure in cotton or the type of yarn used, is difficult to say. For wool, however, significant changes were observed and the results indicate that Coltide HQS improves fibre lubricity and reduces fibre degradation.

7.5 Wettability

It is important that any treatments on certain types of fabrics, e.g. towels, do not significantly impair wetting or moisture absorbency. Wettability of the control and test fabric (15 samples each) was assessed after 1, 5, 10 and 20 wash cycles.

Cotton

The results **(Table 1)** show that the addition of Coltide HQS to a conditioner does not impair the wetting characteristics after 10 wash cycles, and all fabrics 'wet out' immediately. After 20 wash cycles the test fabric is marginally slower to 'wet-out' than the control fabric, although not to the extent that it would present any problems. This suggests the possibility of the protein depositing on the fibre surface and is backed up by the results of the protein deposition study.

Wool

Wettability is not a prerequisite for wool because it is predominantly used to produce outer garments which need to be resistant to wetting. The results show no difference in wettability after 10 wash cycles, between untreated, control and test fabrics, but there is a significant reduction in the time taken to wet-out the fabric after 20 wash cycles for both control and test fabrics. The most probable reason for this is the loss of the Hercosett resin from the surface of the wool fibre; this is also indicated by the SEMs. The wettability study shows that Coltide HQS does not impair or alter the wetting characteristics of the fabrics any more than using a fabric conditioner alone.

		Cotton		Wool	
		Control	Test	Control	Test
Wash cycles	0	15 secs	15 secs	3 mins	3 mins
	10	Immediate	Immediate	3 mins	3 mins
	20	<2 secs	3.3 secs	4.6 secs	6.4 secs

Table 1 Wettability results for cotton and wool

The improvement is due to the small deposition of the protein from the conditioner and also as a result of the protein being substantive to the cotton or wool fibre during the detergent wash cycles. The combined effect gives rise to the above characteristics.

8. Conclusions

This study has shown that Coltide HQS, when added to a fabric conditioner, even at a low inclusion level, exhibits the following important characteristics:

1. Enhances the conditioning properties of fabric conditioners
2. Significantly improves the 'handle/feel'[1] of cotton terry towelling
3. Reduces fibre erosion in cotton and fibre erosion/degradation in wool
4. Increases the lubricity of wool fibres
5. Does not build-up on cotton or wool fibres
6. Does not impair fabric wettability

9. Outlook

Coltide HQS is part of a range of alkyl quaternary derivatives.The chemistries include:

- Coltide HQS
  Stearyldimonium hydroxypropyl hydrolysed wheat protein
- Coltide BQS
  Stearyldimonium hydroxypropyl hydrolysed cotton protein
- Coltide SQM
  Cocodimonium hydroxypropyl hydrolysed silk protein
- Coltide WQM
  Cocodimonium hydroxypropyl hydrolysed wool protein
- Coltide CQS
  Stearyldimonium hydroxypropyl hydrolysed collagen protein

One would expect all the alkyl quaternary derivatives listed to display similar properties. Thus one could infer that Coltide BQS, SQM, WQM and CQS would give the formulator the same benefits as proven by the experimental work for Coltide HQS above. Opportunities for product differentiation through label claims together with enhanced product functionality arise with Coltide BQS (cotton) and SQM (silk) in particular.

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