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A THERMOANALYTICAL STUDY OF TREATED WOOLS

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Previous studies of fibrous keratins have enabled assignments to be proposed for the endothermic processes identified in the relatively complex DTA curve. From this base, the influence of well defined chemical modifications to keratin on their observed DTA curves has been discussed. Wools are specifically treated commercially to improve shrink resistance and machine washability. To achieve these desired characteristics wools are treated, (a) by special oxidative processes, (b) with specific polymers, and (c) by combinations of (a) and (b). The DTA curves of wool samples which have been subjected to each of the three different treatments were reproducibly recorded. The significance of differences between these curves and that for the untreated fibre are discussed. Although characteristic differences in the DTA curves of wools after specific treatments can be distinguished, differential thermal analysis cannot be regarded as a general tool for such treatment characterisation. It is considered that thermogravimetry should offer a greater potential for this purpose.

Of the common textile fibres wools and hairs are the most complex and also the most chemically active. Commercially chemical treatments are applied to improve wools performance in textile end uses by, for example, reducing or eliminating felting shrinkage or by providing permanent press character. Increasing competition from man made fibre production has stimulated the development of durable treatments for machine washability in wool textiles.

From extensive thermoanalytical investigations of dry keratins (wools), assignements have been proposed for the various component endotherms observed in the reproducible DTA curves [1, 2]. The influence of specific definitive chemical modifications of keratin on the shape, size and position of the endothermic processes observed in the DTA curves of Merino wool have been reported [3]. Bearing in mind the complexities of the substrate it was shown that differential thermal analysis could make a contribution to the study of wool structures and their chemical reactions.

In this work thermoanalytical studies are extended to the examination and potential characterisation of both trial and commercial "non-felting" treatments.

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Wool shrinkproof treatments

Wool is chemically and structurally complex. As a generalization wool fibre can be described as possessing outer cuticular layers (scales) surrounding a central cortex. The cuticle can represent up to 10% of the whole. The existence of two types of cell with different thermal and chemical susceptibilities can be recognized in the cortex. When wet wool fabrics are subjected to mechanical action there is a marked tendency for the wool fibres to move preferentially in one direction. Because of the unique cuticular layer on the surface of the wool fibre there is a differential friction effect (DFE) due to the ratchet action of the overlapping scales. The consequences of this effect are that under mechanical action fibres will move preferentially in the direction of their root ends, with progressively larger entanglements as the mechanical action (as in washing) proceeds. This process of cumulative unidirectional migration is called "felting" and is the origin of the major contribution to wool fabric shrinkage on washing. To provide non-felting, shrinkproof character with wool requires, either impairment of fibre movement through an increase in the general fibre-fibre friction level, or the reduction of the differential friction effect of the scales.

Early chemical treatments which were effective in reducing felting shrinkage were oxidative in character, severe, often uncontrolled and uneven. The damage to the cuticle (scale) was such that the DFE was reduced, but often with the development of an unacceptable impaired handle. The extensive damage often penetrated into the central cortex with loss of other (physical) properties. Modern treatments with milder more controlled oxidative processes, which can be applied without extensive fibre swelling, limit the degradation to the scales, and a reduction in the felting propensity can be achieved without significant loss of physical properties or handle. These milder treatments are considered to act more through the softening of the scales and a resultant increased general friction level [4]. Because of the limited degradation, microscopic recognition of the existence of a treatment is extremely difficult and alternative methods for their identification are desired. Recent non-felting processes have concentrated on the "masking" of the wool scales with a thin coating of a polymer either to inhibit fibre movement or to reduce the differential frictional character of the scale surface. The level of polymer treatment is normally only of the order of 1–4%. Polymer treatments on wool are more efficient for shrinkproofing if the wool is given a chemical pretreatment, which itself need have little effect on the felting. The mild oxidative treatments are particularly useful in this respect where they cause (a) softening of the scales, (b) increased receptivity of the fibre for the polymer and (c) alteration of the surface free energy of the fibre to match that of the polymer, thus allowing the latter to spread readily and evenly over the surface. For adequate durable shrink resistance in machine washing, extensive crosslinking of the polymer coating is usually essential. Examples of "mild oxidation", "polymer" and "pretreatment plus ploymer" processed wools are currently examined by DTA.

The samples examined can be classified into two groups, commercial "trial" samples and operational chemical treatments. The former samples were kindly provided by the Dylan Laboratories of Precision Processes (Textiles) Ltd., and the latter by the International Wool Secretariat. The descriptions of each sample are given with the discussion of the observed DTA curves. Where possible a comparison is made between the DTA curves of treated and untreated samples of the same wool. For the polymer treated wools reference DTA curves were also obtained for the "cured" polymer. In order that the presentation of this polymer in these samples matched that with the polymer treated wools as closely as possible, samples of polymer coated glass fibre (inert over the temperature region examined) were used.

Experimental

The Du Pont 900 differential thermal analyser was used throughout. To improve ΔT sensitivity the original preamplifier was modified to enable, at a flick of a switch, a potential ×10 increase in the gain to be available. In practice this modification could only be used to extend the maximum sensitivity of the basic instrument from 0.1° to 0.05°/inch. The sample preparation and presentation followed the procedures previously found necessary for reproducibility. Thorough drying and continuous evacuation were practized to avoid any influence from hydrothermal or oxidative processes and to aid the rapid removal of volatile products from the sample system/environment. The standardized instrumental and experimental conditions are recorded in Table 1. For the polymer and polymer coated glass fibre samples thermogravimetric experiments were performed with 7.5 mg of "predried" substrate heated at 20°/min. with continuous evacuation on the Du Pont 950 thermobalance.

Table 1

Standard DTA instrumental and experimental conditions

Instrument	Modified Du Pont 900 (increased ΔT sensitivity)
Sample Pretreatment:	Soxhlet extraction of fibre with 40°–60° petroleum ether for 24 hours and ethanol fo 6 hours. Vacuum drying from residual solvent at 40°.
Sample Preparation:	Scissor cut, that fraction held between BS 30/60 mesh sieves used. 7.5 mg compressed to 4 mm depth in 4 mm diam tube.
Sanple "in situ" Drying:	2 hours at 146° under continuous evacuation, cooling back to 60° prior to dynamic heating.
Experimental Condition:	Chromel-alumel thermocouples at the "centres" of both the sample and a balanced inert (glass beads) reference. Continuous evacuation at 30 in Hg. Heating rate 20°/minute.
Display:	Temperature difference as a function of sample temperature.

Results and discussion

In order to interpret the changes which occur in wool DTA curves as a consequence of either chemical modification and/or polymer treatment a clear appreciation of the features observed for the untreated reference wool must first be obtained. In Fig. 1 is illustrated the reproducible DTA curve obtained under

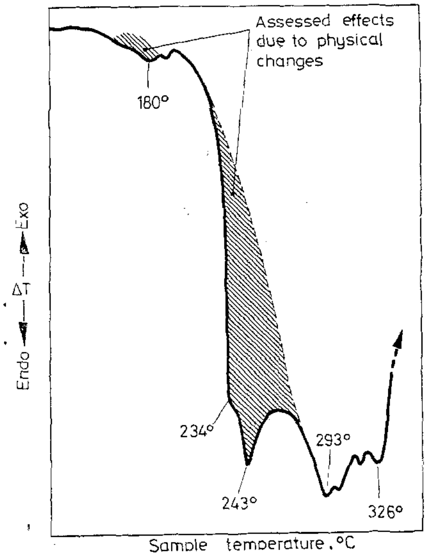

Fig. 1. DTA of 'Predried' keratin fibre; assessed physical changes (continuous evacuation at 30 in. Hg of 7.5 mg and a heating rate of 20°/min)

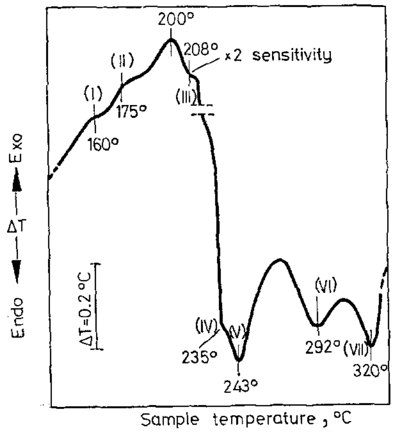

Fig. 2. DTA of "Standard" Merino wool fibre [5] (standard conditions of continuous evacuation, 7.5 mg, 20°/min)

Table 2

Reproducible "Peaks" observed in the DTA curve of predried Merino wool

"Peak"	Temperature of occurrence, °C	Comment
I	160°–168°	Reversible transition, correlated with a physical transition due to onset of side chain motion.
II	171°–194°	Corresponds to a peak in the DTG curve. Chemical in origin.
III	197°–205°	Small shoulder often difficult to recognise due to its proximity to peak IV.
IV	235°	Doublet of peaks due to physical transitions and correlated with loss of α-helical content in keratin, and shrinkage of the fibre.
V	243°	
VI	292°	Peak of a broad endothermal profile reflecting decomposition processes. Starts at about 200°.
VII	321°	"Apparent" peak in the profile of the degradation endotherm.

standard conditions for Merino 64's quality wool, the reference fibre for some of the treated samples examined. In this presented curve of the predried fibre those parts of the observed endotherms which have been correlated with physical transitions have been subjectively shaded. Seven features can be recognized, between 150° and 350° in the reference DTA curve, and these are arbitrarily described as I through VII (see Fig. 2). In Table 2 interpretations are given to these features on the basis of previously reported [1, 2] and subsequent work [5].

"Dylan" commercial test samples

Sample *F* represented the untreated reference wool. All fibre samples were handled in the top form. Samples *A*, *B*, *C*, *D*, *E* and *G* reflect mild oxidative treatments. A polymer treated wool is represented by sample *H*, with which the applied prepolymer is then crosslinked; in this case no improvement in the shrink resistance compared with the untreated samples was recognised. After a mild oxidation (as in sample *G*) only a small improvement in shrink resistance was reported, (with an undefined shrinkage test an area shrinkage of 40% was described for sample *G* compared with a 50% shrinkage after test of the reference wool). When the same polymer as applied for sample *H* was applied to a sample of the treated wool fibre (as sample *G*) a high degree of shrink resistance was achieved (0% area shrinkage after test); such a sample is represented by sample *I*. The nature of the particular prepolymer applied was not disclosed, but a sample of that material for comparison purposes was provided, and examined by DTA. For all the treated wool samples examined a summary of the specific treatments

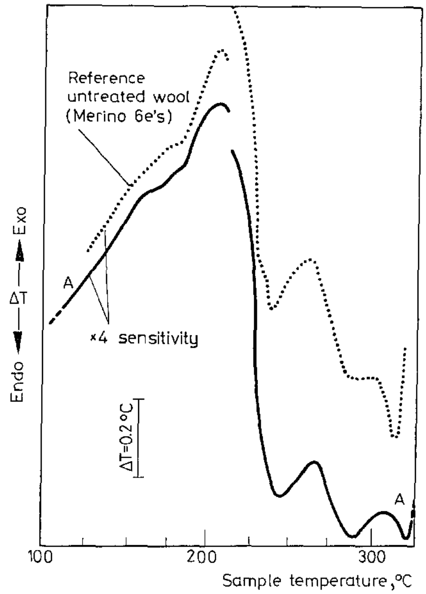

Fig. 3. DTA of treated wools: "Dylan" sample *A*. Chlorination treatment (standard conditions)

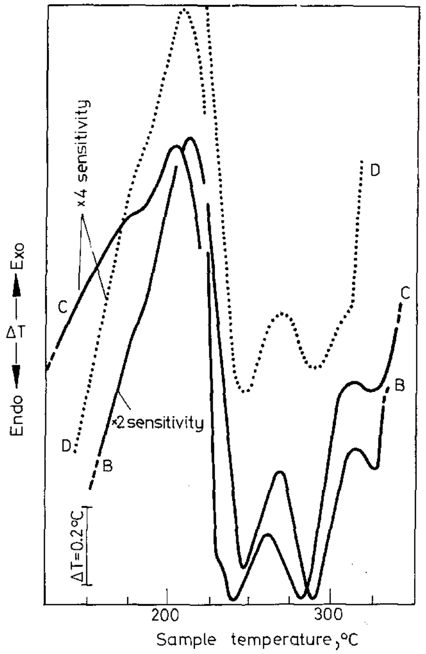

Fig. 4. DTA of treated wools: "Dylan" samples *B*, *C* and *D* (standard conditions). B: treated with permonosulphuric acid, C: treated with DCCA, D: treated with DCCA and permonosulphuric acid

is given in Table 3. Also presented in Table 3 is a summary of the changes in the observed DTA curve "characteristic" features, (IV through VII) identified with these treated wool samples. Representative DTA curves of the treated fibres are presented in Figs 3 to 8. They represent the average observed response from at least two reproducible DTA curves. The detectable differences which arise in the DTA curves as a consequence of the applied treatments were observed in the temperature region 200° to 340°. The major changes in the DTA curves were noticed in the shape and size of the degradation endothermic profiles, "peaks" VI and VII.

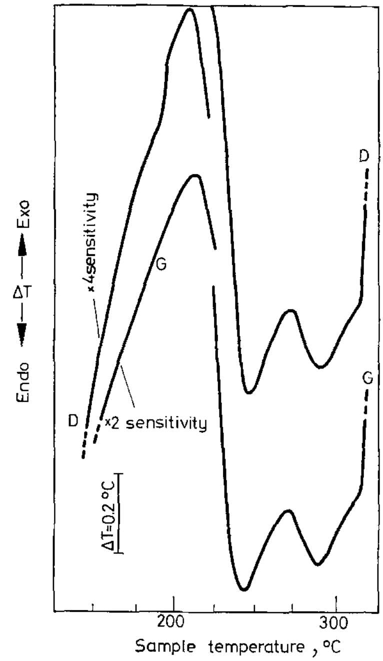

Fig. 5. DTA of treated wools: "Dylan" samples *D* and *G* (standard conditions). Level of treatments: Sample G = 1/3 sampled

These observations are in accord with the previously described changes in keratin DTA curves consequent upon chemical modifications of the substrate [3]. The position of the higher temperature "peak" VII can, as a consequence of dramatic sample movement and collapse, be unreal. To what extent shifts in these "peaks" are due either to the effects of changing overlap and peak size or to more profound changes in the composition of the contributions to the nett degradation profile cannot be ascertained from DTA alone.

Table 3

Observed DTA "Peaks" in wools treated by "Dylan"* processes
(Predried samples of fibre prepared and analysed under "standard conditions". Tabulation reflects the average of more than two determinations)

Sample code	Treatment	Comment	DTA curve observations ("Peaks", °C)			
			IV	V	VI	VII
F	Reference Untreated wool		235	243	292	316
A	2% continuous chlorination (NaOCl/Acetic Acid) at pH = 4 4 seconds exhaustion	Oxidative	235.5	248	291	325
B	"Stevenson X"; permonosulphuric acid (2%) continuous process	Oxidative	238	248.5	290	325
C	2% DCCA, pH = 3.5 continuous process	Chlorination/oxidation	236.5	247	289	324
D	Mix of *B* and *C* treatments to give equivalent of 2% oxidising agent, pH = 3.5, continuous process	Hybrid of *B*/*C*	237	248	291	314
G	As *D* but lighter (approx 1/3) Continuous process	Oxidative. 40% area shrinkage of fabric compared with 50% by reference	237.5	245	290	336
E	"Stevenson *Z*"; alkaline permanganate plus NaOCl. Continuous process	Oxidative	236	248	292	313
H	2.5% crosslinked polymer applied from aqueous alkali	resin treatment 50% area shrinkage compared with 50% by reference	236	244	292	323
I	Treatment *G* plus 2.5% polymer	resin treatment plus pre-oxidation. 0% area shrinkage compared with 50% by reference	236	243	293	325
Prepolymer	As used for *H* and I	Polymer examined alone	"Peaks" observed at 276° and 361°			

* "Dylan" is the trade mark of the Dylan Laboratories of Precision Processes (Textiles) Ltd., Ambergate, Derby, UK.

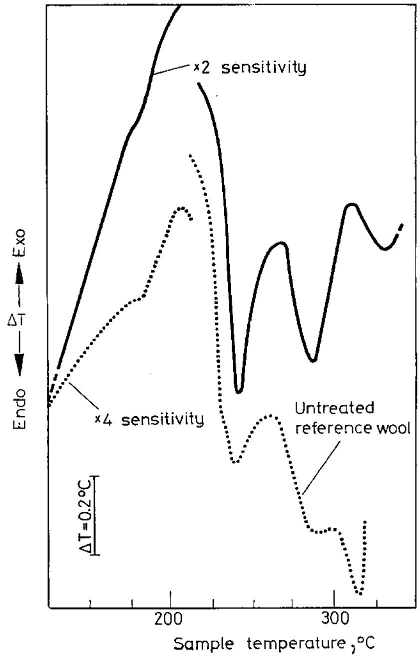

Fig. 6. DTA of treated wools: "Dylan" sample *E*. Shrinkproofing process (standard conditions)

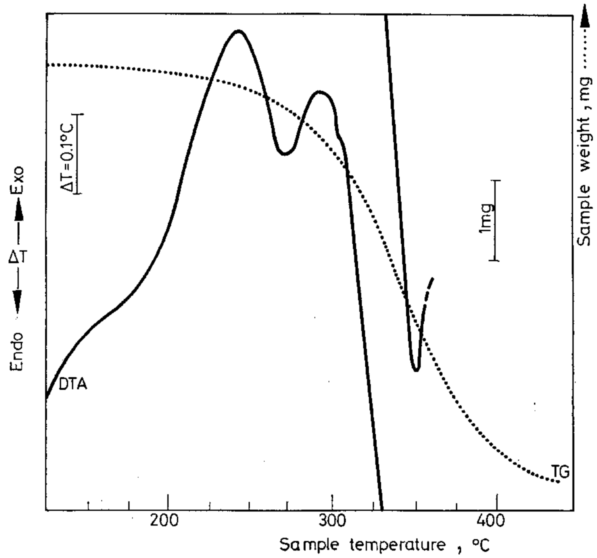

Fig. 7. Thermal analysis of "Dylan" prepolymer. (DTA and TG with 10 mg samples, 20°/min, continuous evacuation)

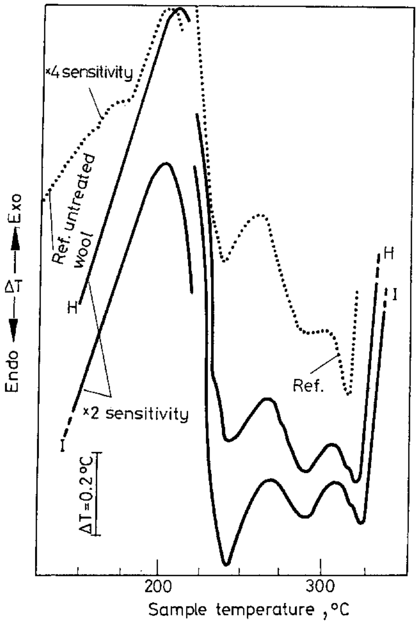

Fig. 8. DTA of treated wools: "Dylan" resin treated samples *H* and *I* (standard conditions) "Dylan" *H*: resin applied to untreated wool; "Dylan"*I*: resin applied to pretreated wool

The "peaks" IV and V attributed to physical transitions (disordering of the α-helical elements) are still identifiable after the oxidative treatments. These α-helical elements are located primarily in the microfibrils of the cortical cells. Previously reported oxidations of keratin fibres with performic acid involved the oxidation of helix stabilizing cystine bridges with marked reduction and loss of the IV and V "peaks" [3]. It could be suggested from these observations that these mild treatments have either not penetrated to the cortical regions, or have caused little degradation to the helical material. With sample *A*, broadening of the IV, V doublet was subjectively recognized (Fig. 3).

With the oxidative treatments *A* and *B*, the higher temperature part of the doublet apparently shifted to higher temperatures, an observation also noted with the oxidative treatments *C*, *D* and *E* (Fig. 4). Sample *C* is a mild oxidation treatment which has been the subject of particular commercial activity. Dichloroisocyanuric acid (DCCA) allows for a strictly controlled chlorine release and oxidation: DCCA + $2H_2O \rightarrow 2HOCl$ + isocyanuric acid. Cosnard [6] has reported that treatment of Merino wool at p_H 4 with DCCA resulted in a product that showed a decrease in the "ortho" cortex type content and an increase in that fraction which reflected "para" cortex type behaviour. Too great a significance cannot be attributed to these observed changes in the doublet because of the noted variations in the shape of the overlapping broad degradation endotherm (VI). The unknown polymer applied as a treatment with samples *H* and *I* was also examined separately. The "prepolymer" was a rubbery mass which "dried" to a brittle solid on treatment at 80° under vacuum. The DTA and TG curves of the polymer are shown in Fig. 7. The major movements in the DTA curve "peaks" at 276° and 361° are clearly associated with chemical changes. When wool samples treated with this polymer were examined, no distinct endotherms, which could be identified as specific to the polymer, were obtained either with, (*I*), or without, (*H*), pretreatment of the wool (see Fig. 8). The polymer chemical change endotherms would be lost within the keratin DTA degradation profiles. Although the precise nature of this polymer was not known the DTA curve obtained was almost identical to that observed for a 100% sample of the "Kymene" commercial polymer, see below.

Commercial "shrinkproofed" wools

Three different shrinkproof treatments involving polymer treatments applied to wool were examined. The DTA curves of the treated fibres are presented in Figs 9, 11 and 13 and the DTA/TG curves of the relevant polymers (applied to glass fibre substrates) are shown in Figs 10, 12 and 14.

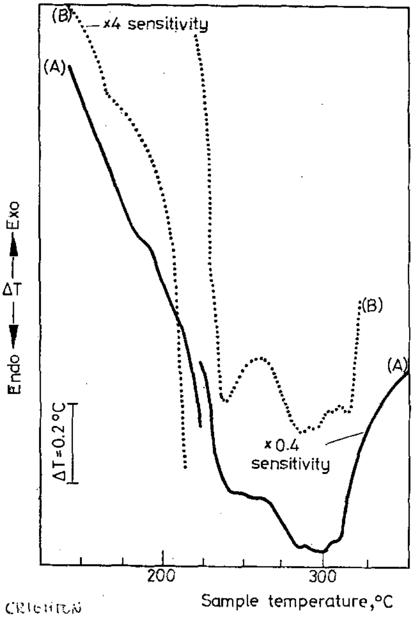

Fig. 9. DTA of treated wools: "Synthrappret LKF" on wool (standard conditions) *A*: Synthrappret LKF on Merino top. *B*: Synthrappret LKF on reduced Merino top

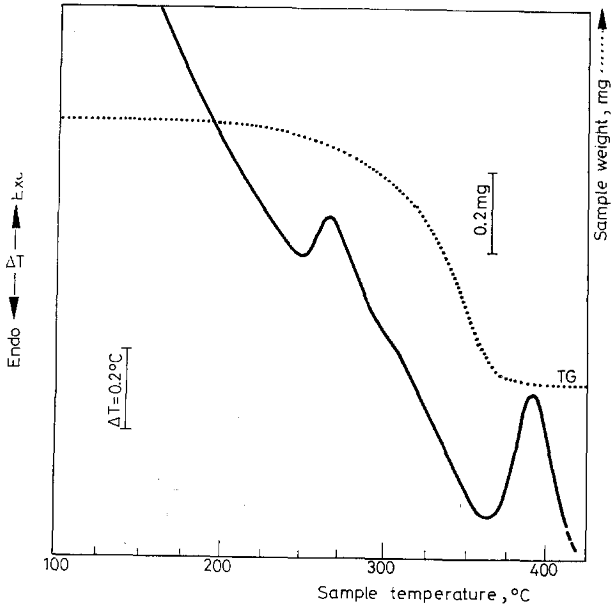

Fig. 10. Thermal analysis of "Synthrappret LKF" (standard conditions for DTA and TG, with resin applied to a gass fibre substrate)

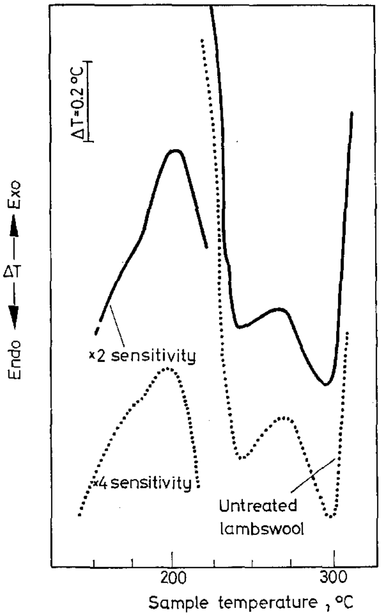

Fig. 11. DTA of treated wools: "Zeset TP" on lambs wool (standard conditions). (Observations with a treated and an untreated wool sample)

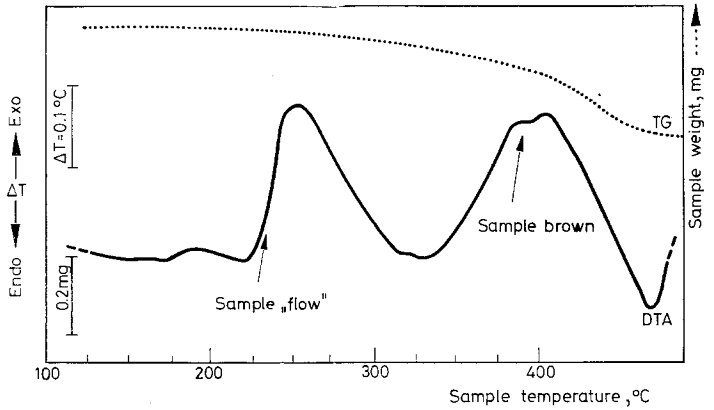

Fig. 12. Thermal analysis of "Zeset TP" (standard conditions for DTA and TG, with resin applied to a glass fibre substrate)

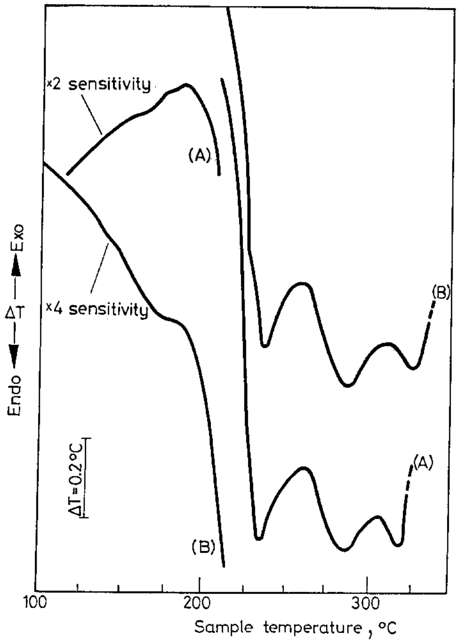

Fig. 13. DTA of treated wools: "Kymene 567" on wool (standard conditions). *A*: 1.9% "Kymene 567" on wool. *B*: 2.5% "Kymene 567" on chlorinated Merino top

acceptable stability to repeated machine washings is to be obtained. The level of polymer treatment is normally between 1–4.5% [7].

Generally the polymer finishes are applied on wool as "soluble" prepolymers and must either be grafted to the wool or cured to a high crosslink density if

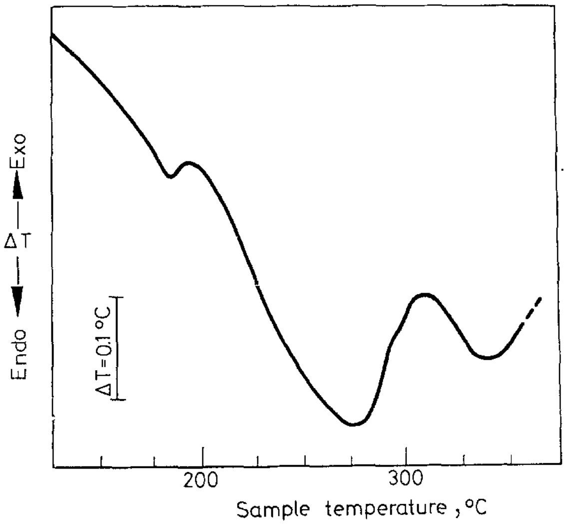

Fig. 14. DTA of "Kymene 567" resin (standard conditions, resin applied to a glass fibre substrate)

The "Zeset TP" (Du Pont) polymer is a reactive polyolefin probably containing acid chloride groups [7]. The DTA/TG curves (Fig. 12) of the resin-glass fibre system showed the effects of sample system instability due to polymer flow, as well as degradation. No interpretation is ventured for the DTA curve movements below 300° because of the noted instabilities. In Fig. 10 is recorded the DTA and TG curves of "Synthrappret LKF" (Bayer) resin applied to a glass fibre support. This prepolymer is a low molecular weight isocyanate terminated polyurethane which, on wool, in the presence of labile hydrogens yields via a substituted urea, a crosslinked polyurethane – urea. Curing can be achieved by a variety of agencies including heat [8]. A subjective assessment of the DTA curve of Synthrappret LKF on glass fibre in the absence of further information (except for the TG curve) suggests that two endothermic profiles are present with observed "peaks" at 245° and 360°. "Kymene 567" is a water soluble branched polyamide-epichlorhydrin mixture system. This system will yield through an azetridinium compound a crosslinked and grafted resin film on wool [9]. The azetridinium entity will react with nucleophilic groups in the prepolymer (secondary and tertiary amines) to provide crosslinking and with thiol and amino groups of wool to generate the grafting link. In Fig. 14 is shown the DTA curve of the resin applied to glass fibre; endothermic effects are reflected in the "peaks" observed at 275° and 330°. Examination of an unsupported sample of the polymer provided as a film lead to DTA curves which were difficult to reproduce due to problems of sample presentation of fine film pieces in the DTA sample tube and the resulting instability observed in the temperature range up to 200°.

Comparisons of the DTA curves of polymer treated wools with the appropriate reference wools and with the resins supported on glass fibre were attempted. In the DTA curves of treated wools no clear peaks specific to the applied polymer could be detected by "curve-overlay" methods. A suggestion of a peak on the Kymene treated sample and of a lower temperature degradation/collapse for the Synthrappret treated wool were noted. The characteristic DTA features of the resins are basically associated with chemical changes and are found in the same temperature regions as the degradation profiles of the substrate wool. It is not entirely surprising therefore that their observation on wools was precluded. Difficulties might also be expected in the attempted comparisons, from the fact that the necessary thermally inert support (glass fibre) for the reference DTA curves of the resin, will mean that the "curing" chemistry in these systems will not be identical to that which occurs in the presence of wool.

Conclusions

When chemical treatments alone are used to produce anti-felting characteristics in wool, their existence is reflected in subtle changes in shape to the degradation profiles of the DTA curves of predried samples. Although these changes are reproducible and characteristic, their use alone for identifying the nature of the chemical treatment cannot be considered as practical.

Many of the commercial shrinkproofing treatments involve the application of resins either with or without wool pretreatment. To achieve durable and effective treatments most of the applied resins are crosslinked. Recognition of specific polymers by DTA rests on the identification of a characteristic degradation profile. The positions of these degradation endotherms overlap the degradation endotherms of wool and, unless the magnitude of the heat effect is very large, their observation depends on the ability to observe subtle changes in the wool endothermic profiles.

The samples from test commercial treatments should not necessarily be interpreted as directly related to current "Dylan" commercial processes. At the same time, commercial processes do reflect the principles, and cover the types, of treatments examined.

The existence of a chemically modified wool can be recognised from the changes in the DTA curve compared with that for an untreated wool. However, because of the empirical character of DTA, the definitive nature of any applied treatment cannot be identified without supplementary supporting information.

Differences in the DTA degradation profiles arise as a result of all the types of treatments applied. The conventional DTA arrangement and sample containment conditions precludes detailed information being obtained from such broad multicomponent degradation profiles. It is suggested that with thermogravimetry, where the sample presentation and operating conditions can be controlled to close to the optimum requirements for degradation characterisation, a more practical general procedure exists for the recognition of shrinkproofing and other treatments applied to wool.

We wish to thank Precision Processes (Textiles) Ltd., and the International Wool Secretariat for samples and information. Their co-operation is gratefully acknowledged. One of us (WMF) wishes to record her thanks to the I.W.S. for their support of a research studentship.

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RÉSUMÉ — Des études antérieures sur les kèratines fibreuses ont permis de proposer des interprétations sur les effects endothermiques identifiés sur la courbe ATD relativement complexe. Sur cette base, l'influence de modifications chimiques bien définies de la kératine sur les courbes ATD observées est discutée. Les laines, à l'échelle commerciale, sont traitées spécifiquement pour augmenter leur résistance au rétrécissement ainsi que pour améliorer leur faculté de lavage en machine. Afin d'atteindre ces caractéristiques, elles sont traitées soit par des procédés oxydants spéciaux, soit par des polymères spécifiques soit par les deux. Les courbes ATD d'échantillons de laines traitées par chacune de ces méthodes ont été enregistrées de façon reproductible. Les différences observées entre les courbes obtenues avec les fibres traitées et non traitées sont discutées. Malgré des différences caractéristiques, l'analyse thermique différentielle ne peut pas être considérée comme une méthode universelle pour caractériser de tels traitements. La thermogravimétrie pourrait être potentiellement plus adaptée.

ZUSAMMENFASSUNG — Vorangegangene Untersuchungen über faserige Keratine ermöglichten Zuordnungsvorschläge für die in der verhältnismässig komplexen DTA-Kurve befindlichen endothermen Vorgänge. Auf dieser Basis wurde der Einfluss gut definierter chemischer Veränderungen in Richtung Keratin auf ihre beobachteten DTA-Kurven erörtert. Die Wollen werden im Handelsmaßstab spezifisch behandelt um ihre Widerstandsfähigkeit gegenüber dem Eingehen zu erhöhen und ihre Waschbarkeit in der Maschine zu fördern. Um diese erwünschten Charakteristika zu erreichen werden die Wollen a) durch spezielle Oxidationsvorgänge, b) mittels spezifischer Polymere und c) mit kombinierten Verfahren von a) und b) behandelt. Die DTA-Kurven von jedem dieser drei verschiedenen Behandlungen unterworfenen Wollproben wurden reproduzierbar aufgezeichnet. Die Signifikanz der Unterschiede dieser Kurven gegenüber denen der unbehandelten Fasern wird erörtert. Obwohl sich charakteristische Unterschiede in den DTA-Kurven der spezifisch behandelten Wollen beobachten lassen, kann die Differentialthermoanalyse nicht als ein allgemein anwendbares Verfahren zur Charakterisierung solcher Behandlungen betrachtet werden. Es wird angenommen, dass die Thermogravimetrie für diesen Zweck grössere Möglichkeiten bietet.

Резюме — Предыдущее изучение волокнистых кератинов представило возможным дать отнесение эндотермических процессов, идентифицированных на относительно сложной кривой DTA. Исходя из этого, обсуждено влияние хорошо определенных химических изменений кератина на наблюдаемые кривые DTA. Шерсть, для улучшения устойчивости к усадке и машинной мойке, обрабатывалась специфическим образом. Для достижения этих желаемых характеристик шерсть обрабатывалась: а) специальными окислительными способами, б) специфическими полимерами и в) комбинацией методов а) и б). Воспроизводимо сняты кривые DTA образцов шерсти, обработанных этими тремя различными способами. Обсуждено различие между этими кривыми и кривыми для необработанного волокна. Хотя характерные различия кривых DTA образцов шерсти после специфических обработок могут быть определены, однако дифференциальный термический анализ не может быть принят как общий метод для характеристики такой обработки. Считалось, что термогравиметрия должна была бы дать большую возможность для этой цели.