

# Infrared Study of the Effect of Heat on Wool

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## Synopsis

The infrared spectra of wool heated in vacuum and in air to different temperatures ranging from 120 to 250°C were investigated. It was found that certain absorption bands disappear when wool is heated in vacuum to 180°C and in air to 120°C for 2 hr. Also, the results showed that the intensities of the C=O stretching band at 1660  $\text{cm}^{-1}$ , N-H stretching band at 3325  $\text{cm}^{-1}$  and the C-H stretching band at 2940  $\text{cm}^{-1}$  decrease when wool is heated in vacuum to 180°C and in air to 120°C. The spectra of the samples heated in vacuum to 250°C and in air to 225°C exhibited strong absorption bands belonging to the carboxyl and sulfonate groups.

## INTRODUCTION

The study of heat effects on wool has both fundamental and applied interest. It is well known that the physical properties of wool are influenced by thermal pretreatments. Indeed, the specific changes produced when wool is subjected to heat have been shown to depend not only on temperature but also on the time of treatment and other conditions of heating such as the presence of oxygen.

Several researchers<sup>1-4</sup> have shown that in the lower temperature range the only important change in wool is drying; this dominates to about 120°C. Other workers<sup>5-7</sup> have found that in the range 140–170°C the concentration of acid and base groups both decrease, leading to the notion that amide crosslinks are formed between them. As the temperature is raised above 170°C, the solubility of wool in sodium bisulfite begins to increase indicating a more general thermal breakdown. At higher temperatures, however, wool undergoes a sort of melting which has been put at 240°C.

The present study is undertaken to investigate the effect of thermal treatments under various conditions (in vacuum and in air) on the molecular structure of wool. The changes in the molecular structure were determined by studying the corresponding changes in the infrared spectra of the treated samples.

## EXPERIMENTAL

Wool fibers from four breeds such as Merino, Barki, Osimi, and Rahmani were used. The sheep are of nearly the same age ( $\approx 2$  years) and are grazed on the same land under the weathering conditions of Egypt. The Rahmani wool is characterized by its brownish color, the Osimi is white-cream, and both Merino and Barki wools are white.

Scouring of raw wool was carried out by using the method of Fincham.<sup>8</sup> First, the fibers were rinsed in water and extracted in soxhlet apparatus with ether for 24 hr, then with ethanol for the same period. Second, the fibers were washed

with distilled water and left to dry in open air. Finally, they were washed with 3 g/liter solution of nonionic detergent Hostipal CV (Hoechst) for 1 hr at 25°C and then by distilled water until free from detergent. The fibers were subsequently dried in an electronic oven at 70°C for about 24 hr.

In measuring wool fineness, the air flow method was used. Also the gravimetric method<sup>9</sup> was used for measuring the moisture contents.

The ashing method used is that of ASTM.<sup>10</sup> In this method 5 g of the wool samples were initially charred in a crucible until no more volatile matter was produced; this was followed by ignition in a muffle furnace at 650°C for 6 hr until carbon had been burned off. After ashing had taken place the ash samples were cooled in a desiccator for 4 hr or more. Sample weight was determined using a macrobalance.

The extensively dried fibers were cut into small pieces and ground in a hardened steel vial containing two steel balls. The vial was fitted to a Spex-mixer mill which was rotated for short periods. The grinding process was carried out several times for short periods in order to avoid the oxidation of the samples.<sup>11</sup> The powder was then served to a particle size of a fraction of diameter ranging from 0.053 to 0.297 mm.

A part of the powder was heated in sealed evacuated glass tubes ( $10^{-2}$  torr) in a well-calibrated electric furnace. Another part was heated in air.

A weight of the powder was weighed accurately into a small polystyrene tube. This weight was thoroughly mixed with KBr to give concentration of sample to KBr of 1.5%. The tube was then clamped in the holder of the Wig-I-Bug mixer for about 2 min. A weight of 200 mg of the KBr sample mixture was pressed under vacuum into transparent disks. The infrared spectra (IR) were recorded on the Beckman IR 4220 infrared spectra photometer.

It seems very important to mention here that the obtained intensities of the infrared absorption bands are the averages of three replicate runs. The accuracy of the measured values was found to be 2%.

## RESULTS AND DISCUSSION

The infrared spectra of wool samples from the different breeds of sheep are shown in Figure 1. It could be seen from this figure that the intensities of the absorption bands vary from breed to breed, and the most intense absorption bands are shown in the spectrum of Merino wool, while the less intense bands are shown in the spectrum of Rahmani wool. Both Osimi and Barki wools exhibit absorption bands of intermediate intensities.

A brief summary of the structural assignments for the characteristic absorption bands found in the literature will be given.

The two bands at 3325 and 3075  $\text{cm}^{-1}$  were assigned as N—H stretching vibrations.<sup>12-17</sup> The three absorption bands at 2960, 2940, and 2875  $\text{cm}^{-1}$  were assigned to the asymmetric and symmetric  $\text{CH}_3$  and  $\text{CH}_2$  stretching vibrations.<sup>12-17</sup> The bands at 1600 and 1525  $\text{cm}^{-1}$  were assigned to the C—O stretching vibration and N—H bending vibrations, respectively.

The three bands at 1450, 1400, and 1240  $\text{cm}^{-1}$  seem to have been recognized as characteristic protein bands. The first band is usually assigned to the well-known characteristic deformation frequency of  $\text{CH}_2$  and  $\text{CH}_3$  groups. The band at 1400  $\text{cm}^{-1}$  was assigned to the lower  $\text{COO}^-$  absorption frequency.<sup>15</sup> The 1240  $\text{cm}^{-1}$  band was assigned as N—H deformation frequency.<sup>12-17</sup>

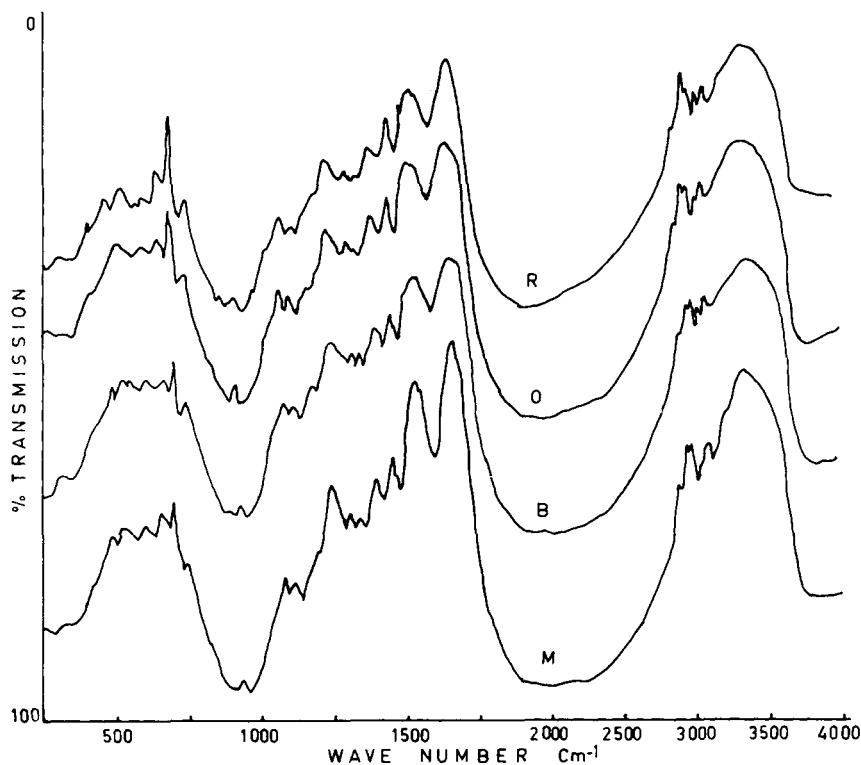


Fig. 1. IR spectra of Rahmani (R), Osimi (O), Barki (B), and Merino (M) wools.

The remaining bands at 1340 and 1075  $\text{cm}^{-1}$  were assigned as N—H deformation<sup>18</sup> and R—SO<sub>2</sub>H vibrations, respectively.

Previous investigations of the IR spectra of oxidized keratin have revealed that all the oxidized species absorb at 1040  $\text{cm}^{-1}$  and in some cases an absorption band at 1175  $\text{cm}^{-1}$  also appears. This led to the conclusion that the presence of the 1175  $\text{cm}^{-1}$  band indicates the formation of sulfonate or sulfonic acid and the occurrence of the band at 1040  $\text{cm}^{-1}$  was indicative of sulfoxide group.<sup>14-17,19</sup>

However, Harvey and Bit-Alkhas<sup>19</sup> stated that the principal change in the IR spectra caused by the oxidation of hair is the appearance of new bands at 1175 and 1040  $\text{cm}^{-1}$ . This statement is in agreement with the information reported by Robbins<sup>17</sup> who observed these two bands at 1040 and 1175  $\text{cm}^{-1}$  in the IR spectra of oxidized keratin and concluded that the oxidation of disulfide to sulfonate is a major transformation in this reaction. However, these results do not

TABLE I  
Intensity of the C—O Band at 1660°C for Wool

Breed	$\log I_0/I$	$\Delta\nu_{1/2}$ ( $\text{cm}^{-1}$ )	$\log I_0/I \times \Delta\nu_{1/2}$
Rahmani	0.181	0.135	24.43
Osimi	0.211	0.125	26.375
Barki	0.208	0.140	29.12
Merino	0.284	0.110	31.24

TABLE II  
Intensity of the N—H Band at 3325 cm<sup>-1</sup> for Wool

Breed	log I <sub>0</sub> /I	Δν <sub>1/2</sub> (cm <sup>-1</sup> )	log I <sub>0</sub> /I × Δν <sub>1/2</sub>
Rahmani	0.099	590	58.41
Osimi	0.146	570	83.22
Barki	0.148	610	90.28
Merino	0.161	580	93.38

TABLE III  
Absorbances of the C—H Stretching Band at 2940 cm<sup>-1</sup> of Wool

Breed	log I <sub>0</sub> /I
Rahmani	0.168
Osimi	0.171
Barki	0.164
Merino	0.171

agree with those reported by Shah and Gandhi.<sup>20</sup> These investigators were unable to detect absorption at 1175 cm<sup>-1</sup> and assigned the band at 1040 cm<sup>-1</sup> to sulfoxide. They also assigned the band at 1370 cm<sup>-1</sup> to —SO<sub>3</sub><sup>-</sup>...<sup>+</sup>H<sub>3</sub>N<sup>-</sup> or SO<sub>2</sub>—NH.

In addition Harvey and Bit-Alkhas noted a decrease in the weak band at 1075 cm<sup>-1</sup> through the course of oxidation and the appearance of a band at 1120 cm<sup>-1</sup> for the three-time oxidized hair. Hence they assigned the band at 1120 cm<sup>-1</sup> to the absorption of cystine dioxide. Furthermore, they mentioned that the ATR spectrum of untreated hair shows absorption at 1040 cm<sup>-1</sup> and perhaps 1175 cm<sup>-1</sup>, indications of the presence of cysteic acid sulfonate residues, at least in the cuticle. Amino acid analysis of such hair shows a cysteic acid content of about 55 μH/g. Presumably this is present as a result of normal air oxidation, for example, as a result of weathering.

Rhodes<sup>11</sup> studied the effect of grinding process on the IR spectrum of keratins. He observed that grinding process produces an absorption band at 1040 cm<sup>-1</sup> which is ascribed to cysteic acid group.

Farland et al.<sup>21</sup> have studied the effect of grinding on the structure of keratins

TABLE IV  
Intensity of the C—O Band 1660 cm<sup>-1</sup> for Wool Heated to 150°C

Breed	log I <sub>0</sub> /I	Δν <sub>1/2</sub> (cm <sup>-1</sup> )	log I <sub>0</sub> /I × Δν <sub>1/2</sub>
Rahmani	0.187	160	29.9
Osimi	0.237	160	37.92
Barki	0.276	165	37.29
Merino	0.264	145	38.28

TABLE V  
Intensity of the N—H Band at 3325 cm<sup>-1</sup> for Wool Heated to 150°C

Breed	log I <sub>0</sub> /I	Δν <sub>1/2</sub> (cm <sup>-1</sup> )	log I <sub>0</sub> /I × Δν <sub>1/2</sub>
Rahmani	0.140	600	84
Osimi	0.160	600	96.0
Barki	0.158	610	96.38
Merino	0.177	570	100.89

TABLE VI  
Absorbances of the C—H Stretching Band at 2940  $\text{cm}^{-1}$  of Wool Heated to 150°C

Breed	$\log I_0/I$
Rahmani	0.147
Osimi	0.174
Barki	0.184
Merino	0.158

and stated that cystine and, to a less extent, tyrosine residues may be destroyed when wool is ground. Although sulfate radicals, cysteic acid, and lanthionine residues have been identified in the product, the degradation produced by grinding is not confined to disulfide bond fission. It could be expected that the molecular fragments produced would undergo further reactions such as oxidations. These reactions would account for the presence of cysteic acid residues and sulfate radicals in ground keratins.

However, in the present study it could be pointed out that the IR spectra of native Egyptian wools exhibit a definite and sharp absorption band at 1120  $\text{cm}^{-1}$  and the detection of this band is without doubt. Also these spectra reveal very weak shoulders (particularly for Rahmani wool), at 1040 and 1175  $\text{cm}^{-1}$  incorporated in the absorption bands at 1075 and 1240  $\text{cm}^{-1}$ , respectively. The existence of these two bands may be due to the grinding process and/or the weathering conditions of Egypt.

The absorbances ( $\log I_0/I$ ) and the half-bandwidth ( $\Delta\nu_{1/2}$ ) of the C—O and N—H stretching bands at 1660 and 3325  $\text{cm}^{-1}$ , respectively, as well as the absorbances of the C—H stretching band at 2940  $\text{cm}^{-1}$  were calculated and are given in Tables I–III. The infrared spectra of the samples under investigation were also recorded after heating them to 150°C for 30 min (Fig. 2). The intensities of the above-mentioned bands are given in Tables IV–VI. Some characteristics of the analyzed samples such as ash content, moisture content, and the mean fiber diameter were determined. The determined values are given in Table VII.

It could be seen from Tables I–VII that the intensities ( $\log I_0/I$ )  $\times$   $\Delta\nu_{1/2}$  of the C—O and N—H bands decrease as the ash contents and moisture contents increase. The absorbances of the C—H bands in the spectra of the different varieties of wool are more or less the same. It was found that heating the samples to 150°C produces remarkable increases in the intensities of the absorption bands. The rate of increase is not the same for the different varieties and different bands. The intensities of the C—O band in the spectra of Osimi, Barki, and Merino became nearly equal. This result means that the intensities of the absorption bands recorded at room temperature and before drying depend on the moisture content of the samples.

Samples of both Merino and Rahmani wools were heated in vacuum and in air to different temperatures, namely 120, 150, 180, 200, 225, and 250°C, for 2 hr. The infrared spectra of the heated samples were recorded. Figures 3 and 4 illustrate the spectra of Merino wools heated in vacuum and in air, respectively.

Figures 3 and 4 indicate the following:

(1) The weak bands at 1120, 1300, and 1350  $\text{cm}^{-1}$  disappeared from the spectra of the samples heated in vacuum to 180°C and in air to 120°C. The first two

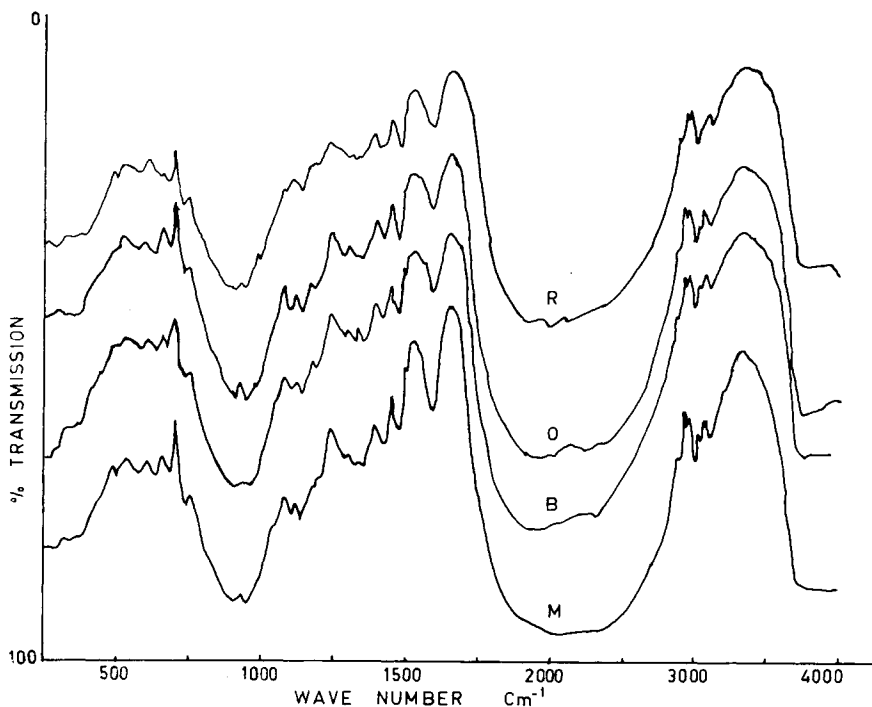


Fig. 2. IR spectra of wool heated to 150°C for 30 min. Letters defined in Fig. 1.

bands were assigned as cystine dioxide symmetric and asymmetric stretching vibrations.<sup>19</sup> The disappearance of these two bands led to the conclusion that they are not due to the absorption of cystine dioxide. This conclusion is not in agreement with that of Harvey and Bit-Alkhas.<sup>19</sup> The third band was assigned to N—H deformation by Habib and co-workers.<sup>18</sup> They concluded that the two bands at 1313 and 1350  $\text{cm}^{-1}$  arise from amide vibrations, and they considered that the N—H vibrations from which these absorptions originate are in side chains of different structural environments.

(2) The band at 1075  $\text{cm}^{-1}$  which belongs to the absorption of R—SO<sub>2</sub>H became less intense in the spectra of the samples heated in vacuum to 180°C and in air to 120°C.

(3) A weak band appeared at 1180  $\text{cm}^{-1}$  in the spectra of samples heated in vacuum to 200 and 225°C, while another weak band appeared at 1040  $\text{cm}^{-1}$  in the spectra of samples heated to 225°C. These two bands at 1180 and 1040  $\text{cm}^{-1}$  appeared in the spectra of the samples heated in air to 200°C. These two bands correspond to the absorption of cystine dioxide S—O and sulfonate—O stretching vibrations, respectively.

TABLE VII  
Some characteristics of Four Egyptian Breeds of Sheep

Breed	Ash content, %	Average diameter	Moisture content, %
Rahmani	2.18	31.4	12.03
Osimi	0.82	31.03	8.70
Barki	0.624	26.4	7.86
Merino	0.450	20.82	6.38

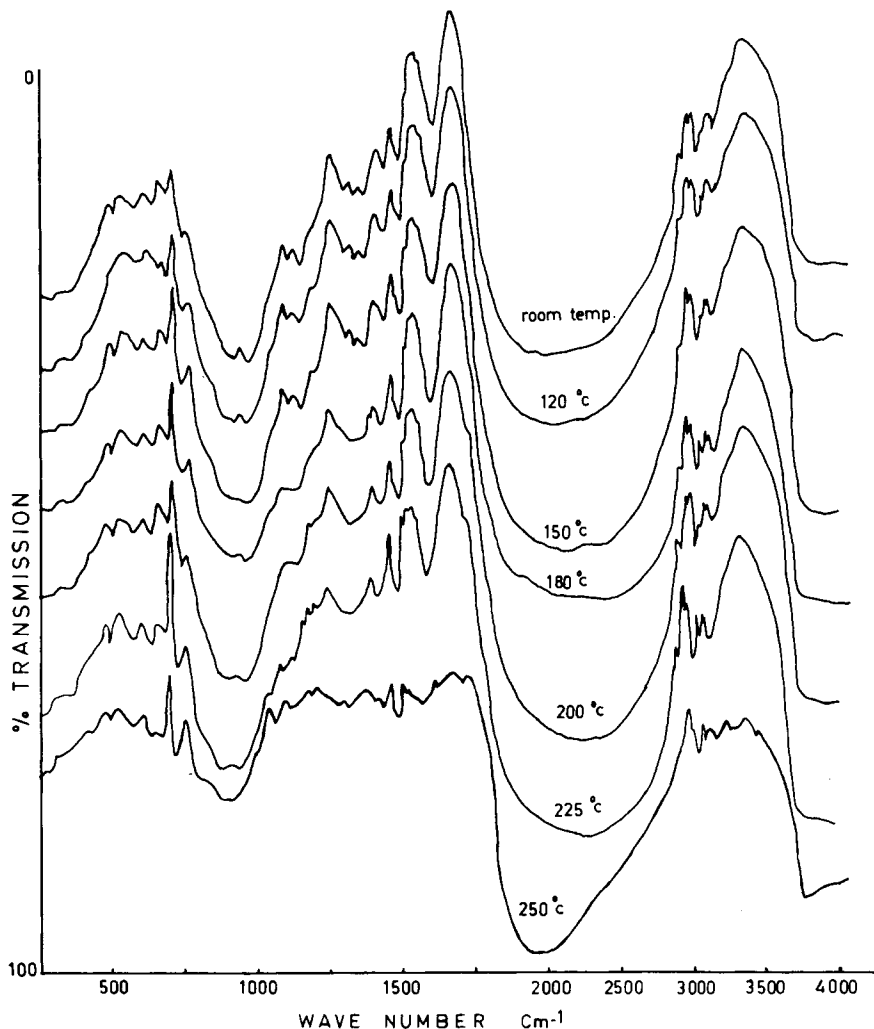


Fig. 3. Effect of heating on IR spectra of Merino wool (in vacuum).

(4) A relatively strong shoulder appeared at about  $1720\text{ cm}^{-1}$  in the spectra of the samples heated to  $200$  and  $225^{\circ}\text{C}$ . This band could be assigned to C—O stretching vibration of carboxyl groups.

(5) The intensities of the bands at  $1240$  and  $1400\text{ cm}^{-1}$  showed remarkable decreases as the temperature increased. The first band is due to N—H deformation and the second is due to  $\text{COO}^{-2}$ .

(6) The spectra of the samples heated in vacuum to  $250^{\circ}\text{C}$  and in air to  $225^{\circ}\text{C}$  could be easily distinguished from those of other heated samples. In those spectra the bands corresponding to the carboxyl group  $1720\text{ cm}^{-1}$  and cysteic acid groups  $1040\text{ cm}^{-1}$  predominate.

The absorbances ( $\log I_0/I$ ) and the half-bandwidth ( $\Delta\nu_{1/2}$ ) of the C—O stretching band at  $1660\text{ cm}^{-1}$  and N—H stretching band at  $3325\text{ cm}^{-1}$ , as well as the absorbances of the C—H stretching band at  $2940\text{ cm}^{-1}$ , were calculated.

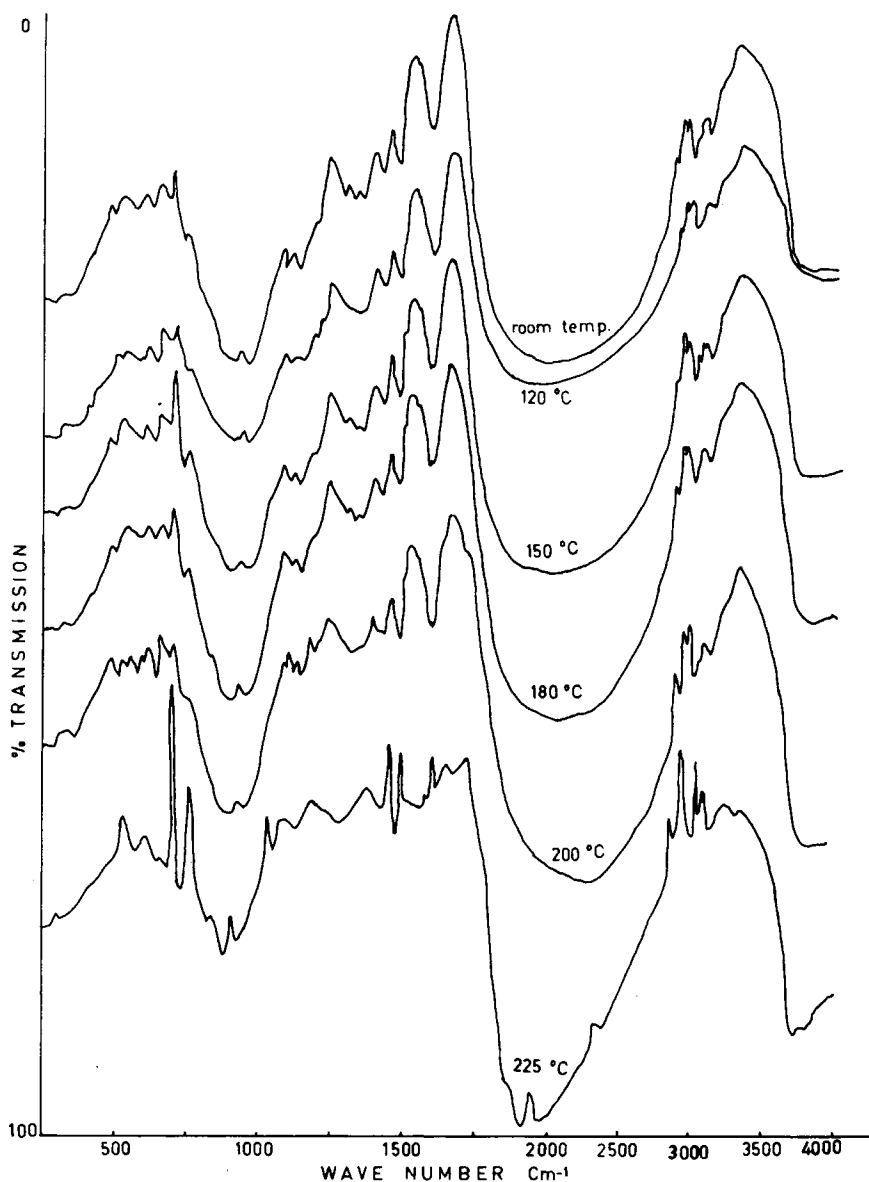


Fig. 4. Effect of heating in IR spectra of Merino wool (in air).

Figures 5-10 show the variation with temperature of the intensities of these bands. It appears from these figures that the intensities of these bands assume considerable decreases after heating in vacuum to 180°C and in air to 120°C.

From the above-mentioned data one can come to the conclusion that the only important change produced in wool when it is heated to 120°C is drying, whereas the changes brought about when it is heated to 150°C are drying, removal of strongly bound water, and a slight change in the amorphous part of protein, in



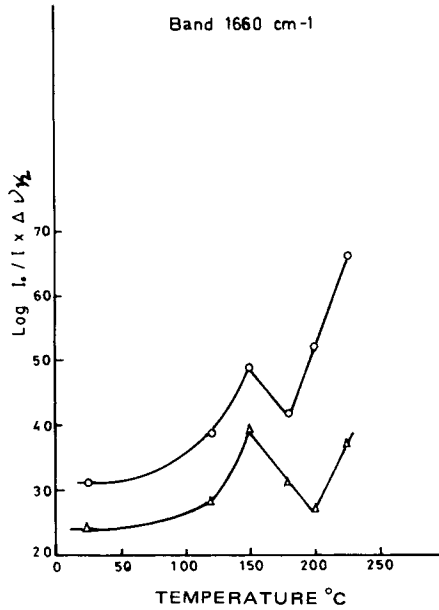


Fig. 5. Variation of intensity of the 1660 cm<sup>-1</sup> IR band with temperature. (O) Merino and (Δ) Rahmani wool.

addition to the probability of formation of amide crosslinks between acid and base groups. The breaking of specific bands of low activation energy and elimination of small molecules from the reactive side chains of the constituent

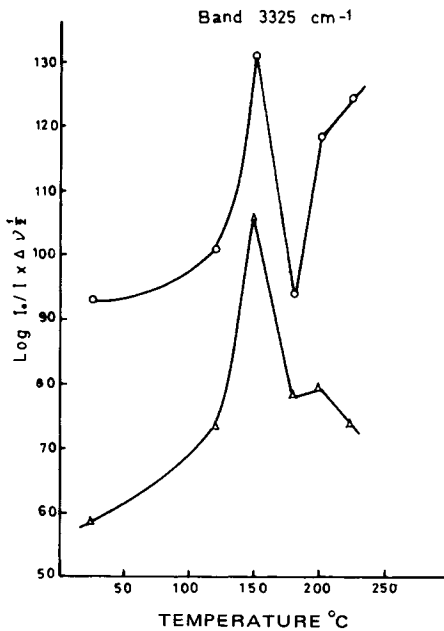


Fig. 6. Variation of intensity of the 3325 cm<sup>-1</sup> IR band with temperature. Symbols as in Fig. 5.

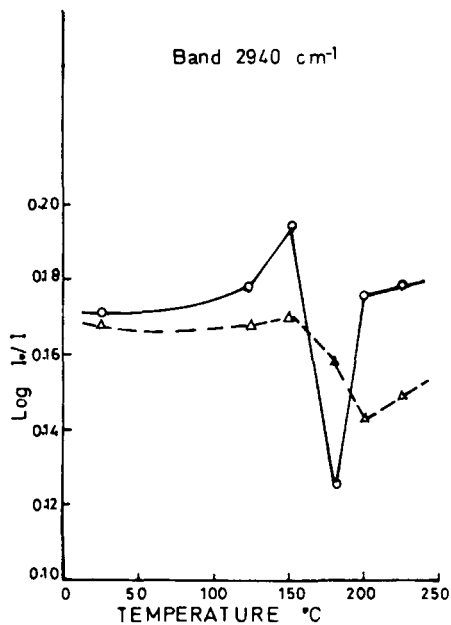


Fig. 7. Variation of intensity of the 2940  $\text{cm}^{-1}$  temperature. Symbols as in Fig. 5.

amino acids occur when wool is heated to 180°C. Also scission of covalent bands, particularly sulfur-sulfur, would be brought about by heating to 180°C. Melting of a small part of ordered wool protein and formation of amide crosslinks in the

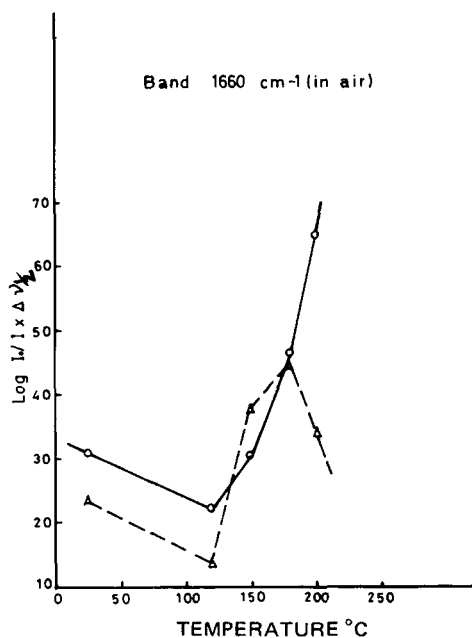


Fig. 8. Variation of intensity of the 1660  $\text{cm}^{-1}$  IR band in air with temperature. Symbols as in Fig. 5.

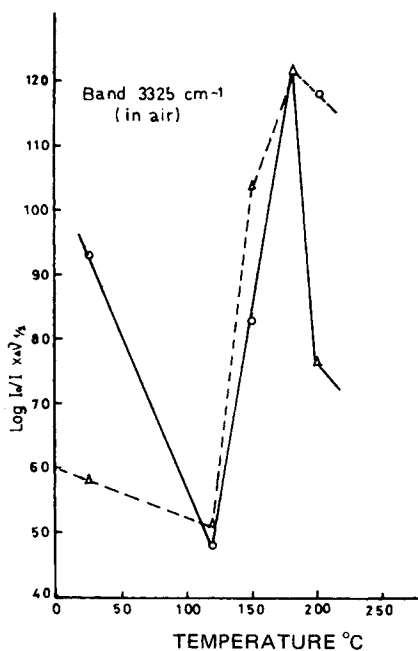


Fig. 9. Variation of intensity of the  $3325 \text{ cm}^{-1}$  in air with temperature. Symbols as in Fig. 5.

newly formed amorphous material would occur by heating to 200 and 225°C. Decomposition of wool by oxidation takes place by heating to 250°C.

The study of the infrared absorption bands of wool samples heated in air led

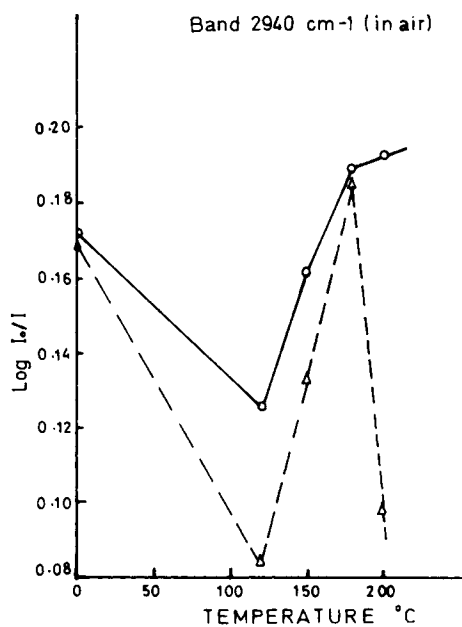


Fig. 10. Variation of intensity of the  $2940 \text{ cm}^{-1}$  IR band in air with temperature. Symbols as in Fig. 5.

to the conclusion that heating wool in air to 120°C results in decomposition of its molecular structure. Heating the samples to 180 and 200°C causes melting of a small part of ordered wool protein and formation of amide crosslink in the newly formed amorphous material. Heating of the samples in air to 225°C causes decomposition of wool structure as a result of oxidation.

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Received November 20, 1979

Accepted March 6, 1980