Acid–Base and Dyeing Properties of Nigerian Merino, Yankasa, and Merino–Yankasa Crossbred Wools

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Synopsis

The acid–base titration curves of three wools, Merino, Yankasa, and a 5/8–3/8 Merino–Yankasa crossbred wool, grown in Nigeria, were measured at 25°C in the presence of varying amounts of sodium chloride. Amino acid analysis was carried out on these wools and correlated with the acid–base properties. The isoionic point and titration curves of Merino and the crossbred wool are similar, while those of Yankasa are somewhat different. The acid–base behavior was interpreted by the Gibbs–Donnan treatment for the acid titrations and the pK_0^1 values for the carboxyl groups obtained, showing the existence of normal and salt-linked carboxyl groups in these wools. Dyeing tests with acidic and basic dyes have shown that the crossbred wool responds almost as well as Merino. Together with the similarity of its mechanical properties, it seems that this crossbred wool is suitable for all the textile applications for which Merino wool is normally preferred.

INTRODUCTION

Sheep breeding experiments involving local and exotic varieties and their crossbreeds were carried out at the former Grassland Research Station, Katsina, Nigeria. Merino sheep, imported in 1960–61 from Rhodesia, were crossed with the local Yankasa sheep, a breed found in the Kaduna, Kano, and Plateau states of Nigeria. This sheep has a coarse fleece with much kemp and medullation, and is classified as a "hair" sheep. Crossbreeds of Merino with Yankasa, and other local varieties, were better able to thrive than Merino under local conditions, and cursory examination of the fleece of Merino–Yankasa crossbreeds showed it to be of high quality as far as appearance and feel are concerned, approaching that of the Merino.

An account of the mechanical properties of the fibers from these Merino, Yankasa, and crossbred sheep, including load–extension curve, breaking properties, diameters, histology, and swelling properties has been given,[1] and has shown a 5/8–3/8 Merino–Yankasa crossbreed to produce wool fibers only slightly inferior to those from the Merino breed.

Here, these wools are compared in respect of their behavior toward acids and bases and acid and basic dyes. Again it is found that the crossbreed closely resembles Merino, while Yankasa is quite different.

EXPERIMENTAL

Wools

Nigerian Merino 64's, Yankasa, and a 5/8–3/8 Merino–Yankasa crossbred wool were used, obtained from the former Grassland Research Station, Katsina, Ni-

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geria. The tips (top one-third) and roots were cut off and the wools given successive extractions in diethyl ether and ethanol, with 40 syphonings at the Soxhlet reservoir. Insoluble dirt was removed manually and the wools was washed eight times with distilled water and dried by centrifugation and with filter paper. The locks were drawn into slivers and chopped into pieces, which were stirred in distilled water, dried, and stored in stoppered bottles in the dark. Before use, the wool was conditioned for at least two weeks at 65% relative humidity and 23°C. Weight of dry wool present was determined on samples by heating to 105°C and weighing.

Reagents

These were B.D.H. analytical-grade reagents, or the best commercially available.

Amino Acid Analysis

Conditioned wool samples, 0.250 g, were hydrolyzed for 18 h in 10 cm^3 5.7 *M* HCl under reflux. HCl was removed by rotary evaporation at 35°C after filtration.

The residue was thrice treated with distilled water and rotary evaporated. It was dissolved in 25 cm^3 distilled water and 0.1-cm^3 samples were used for analysis, with 0.2×10^{-6} mol norleucine as internal standard. A Technicon model NC-I automatic amino acid analyzer was used with a hydrazine–ninhydrin reagent and spectrophotometric determination at 570 nm except for proline, which was done at 440 nm. Tryptophan and free ammonia were not determined.

Isoionic Point

The method of Lemin and Vickerstaff[2] was used, which is based on the change in pH brought about by addition of neutral salt. Duplicate samples of conditioned wool (1.000 g) were placed in 50 cm^3 of an appropriate aqueous HCl or NaOH solution and the equilibrium pH measured. The pH was measured again after addition of 0.100 g NaCl after three to four days at 25°C with continuous shaking. A Pye model 290 pH meter was used calibrated against potassium hydrogen phthalate buffer (0.05 *M* at 25°C is pH 4.01). If the equilibrium pH value is in the neutral region, the shift of pH due to the addition of salt varies linearly with the internal equilibrium pH value. The isoionic point is the pH value which corresponds to zero variation in pH ($\Delta pH = 0$) and can be accurately determined by simple extrapolation.

Acid–Base Titration

Before each titration, the conditioned wool samples (1.000 g) were adjusted to their isoionic points by immersion in a large volume of very dilute aqueous HCl for 24 h, followed by washing in successive large volumes of distilled water until the pH reached and remained at the isoionic point. These samples were dried by filter paper and stored at 65% relative humidity and 25°C until required.

Samples of this wool, 1.000 g, were added to 50 cm^3 aqueous HCl or NaOH of appropriate strengths (when exact strength had been measured either from the pH or by titration in stoppered polythene bottles. These were kept three to four days at 25°C to reach equilibrium, and the acid or base strength was measured again either by pH or titration. The Pye model 290 pH meter was used. Sodium hydroxide solutions were carbonate and CO_2 free; pH measurements were generally done between pH 2 and 11; and titrations, outside that range. The acid or base combined with the wool was calculated from the difference of the two readings.

Dyeing Tests

Naphthalene Black (12.B) and Orange II (C.I. Acid Orange 7) were selected as representative acid dyes with Bismark Brown and Crystal Violet as basic dyes. The procedure of acid dyeing was used[3] with dye at 1% by weight of the fibers, at a temperature of 70°C and with the addition of anhydrous sodium sulfate (8.8%) and concentrated sulfuric acid (2%). For results at pH values of 4 and 9.5 for basic dyes, appropriate buffers were used. All dyeings were carried out at a 50–1 liquor–wool ratio with manual stirring. The spectra were measured on a Pye-Unicam SP 800 UV spectrophotometer, and the percentage exhaustion of the dyebath was calculated.

RESULTS AND DISCUSSION

Amino Acid Composition

Table I shows the amino acid[1,4] composition of the three wools studied. The results are the means of triplicate determinations and are accurate to 5% for each

TABLE I
Amino Acid Composition[a]

	Merino wool		Crossbred wool		Yankasa wool	
Amino acid	a	b	a	b	a	b
ASP	566	64	555	69	545	67
THR	602	68	538	67	438	60
SER	1014	115	910	113	860	106
GLU	944	109	870	108	1180	146
PRO	663	75	500	62	529	65
GLY	678	76	710	88	580	71
ALA	479	54	454	56	447	55
VAL	530	60	426	53	421	52
½ CYS	989	111	820	102	725	89
MET	30	3	33	4	41	5
ILE	264	30	214	27	288	35
LEU	640	72	613	76	655	81
TYR	315	36	303	38	217	27
PHE	212	24	219	27	199	25
LYS	253	28	240	30	291	36
HIS	61	7	59	7	59	7
ARG	625	74	570	71	597	74

[a] a = 10^{-6} mol/g[1]; b = residues per 1000.

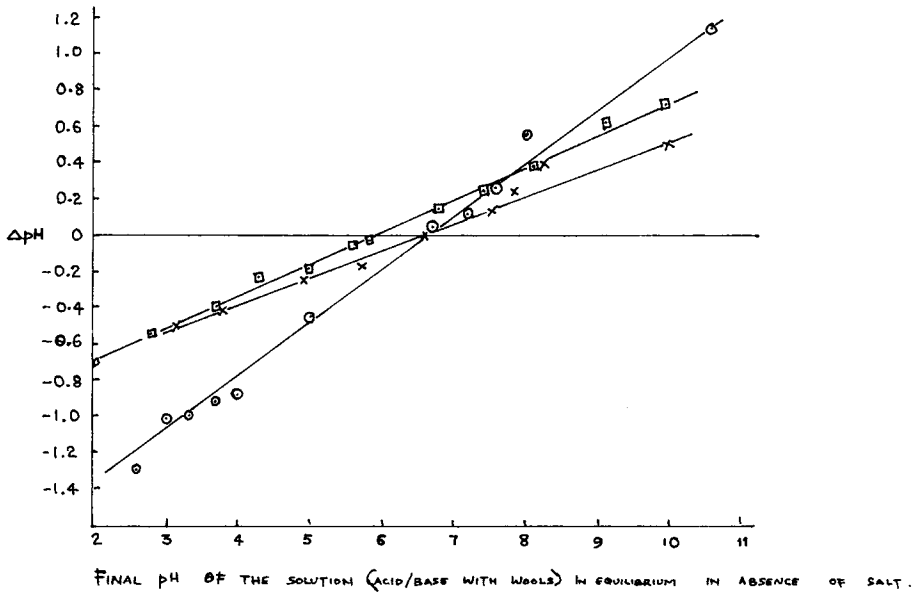

Fig. 1. Isoionic points of wools: (⊙) Merino wool; (X) crossbred wool; (⊡) Yankasa wool.

amino acid. The results for Merino are similar to previous determinations on Australian breed animals.[5,6] Yankasa wool has much more glutamic acid and much less half-cystine than Merino, while the crossbred wool resembles more Merino than Yankasa, except that for half-cystine it is intermediate and for glycine it is higher than either. The totals of acidic amino acids (aspartic and glutamic acids) in Merino, crossbred, and Yankasa wools are respectively 151.0, 142.5, and 172.5 mmol per 100 g dry wool, while the corresponding totals of basic amino acids (arginine, lysine, and histidine) are 93.9, 86.9, and 94.7 mmol per 100 g dry wool for Merino, crossbred, and Yankasa wools, respectively. The latter figures determine the acid uptake of the wools. Other aspects of the amino acid composition have been discussed before.[4]

Isoionic Point

Figure 1 shows the effect on the pH of a solution in equilibrium with the fibers on the addition of neutral salt. The values of the isoionic points obtained were at pH 6.6, 6.6, and 6.0 for Merino, crossbred, and Yankasa wools, respectively, defined as the pH for which addition of neutral salt produces no change in pH. At the isoionic point, all the basic amino acid residues, and an equal number of acidic residues, are charged. The lower value for Yankasa wool reflects the higher number of unionized acidic groups it contains at that point (77.8, as against 57.9 and 55.6 for Merino and the crossbred wools, respectively).

Acid–Base Titration

The titration curves of the three wools with HCl and NaOH at 25°C in the absence of added salt and in 0.1 *M* and 1.0 *M* NaCl are shown in Figures 2, 3, and

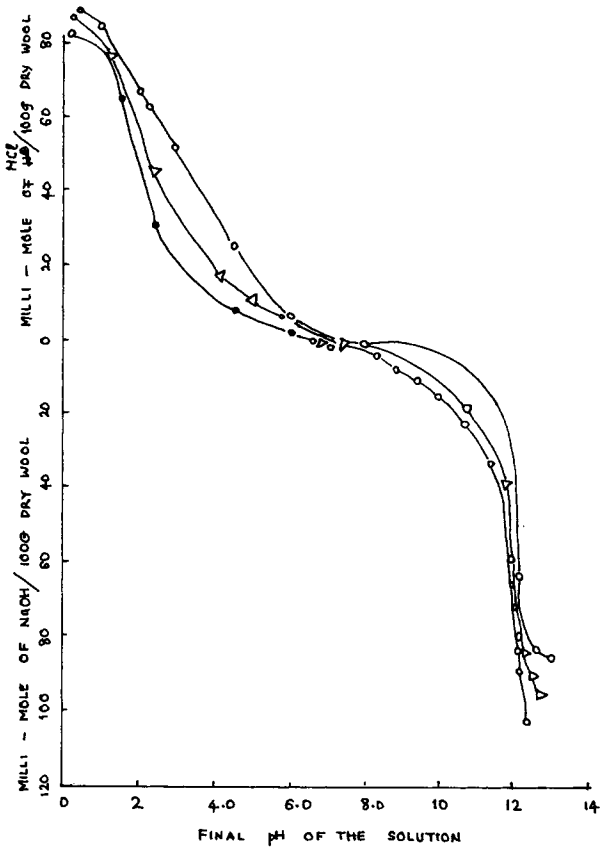

Fig. 2. Acid–base titration of Merino wool at 25°C: (⊙) no salt added; (X) 0.1 *M* NaCl; (⊡) 1.0 *M* NaCl.

4. Increased salt concentration shifts the curves toward neutrality by lowering the electrostatic potential of the fibers. The curves show a maximum acid-combining capacity around pH 0–1 but no clear evidence of a maximum base-combining capacity, due to the onset of hydrolysis. They resemble similar titration curves obtained for other wool samples,[7] as is to be expected.

The maximum acid-combining capacity is 90 mmol HCl per 100 g wool determined from the titration curves, for all three wools. This should be compared with the content of the basic amino acids histidine, lysine, and arginine, since at neutrality only a number of carboxyl groups equal to the number of basic groups can be ionized to preserve electrical neutrality, the extra carboxyl groups being protonated even at neutrality (the very small amount of terminal amino groups is ignored). Within experimental error (5% for amino acid analysis, about 2–3% for titration) these results are in agreement with previous results.

Comparison of the titration curves for Merino and Yankasa wools shows that, relative to Merino, the curves for Yankasa are displaced toward neutrality except at the extremes of pH. The curves for crossbred wool resemble those for Merino wool except that they are closer together between pH 9 and 12. The difference between these curves and those for Yankasa wool are most marked for the acid titration.

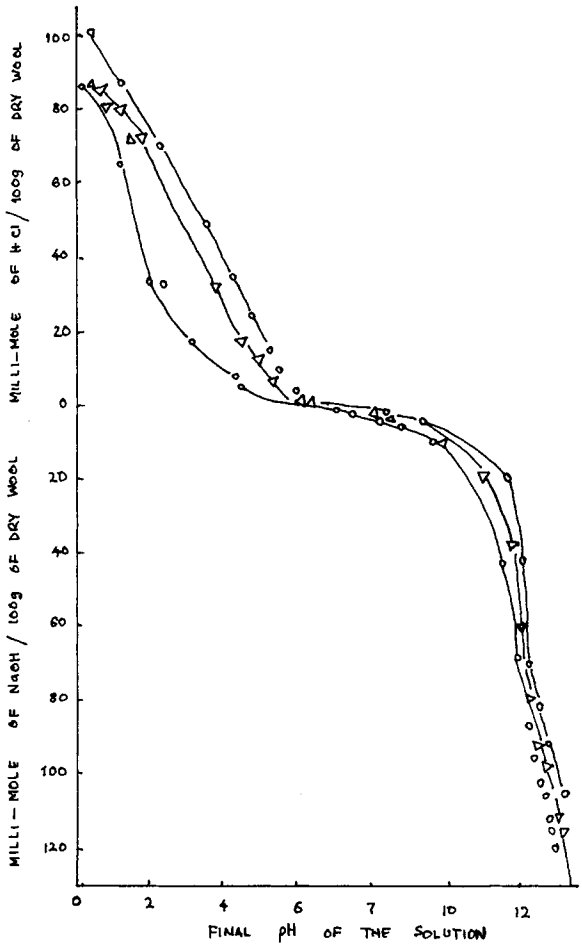

Fig. 3. Acid–base titration of crossbred wool at 25°C: (⊙) no salt added; (X) 0.1 *M* NaCl; (⊡) 1.0 *M* NaCl.

Theoretical Interpretation of the Acid Titration

The Gibbs–Donnan treatment has been successfully applied to the dissociation of fibers by Mathieson and Whewell[8] and to polyelectrolyte resins by Chatterjee and Marinsky,[9] Gustafson,[10] and Mathieson and Shet.[11] If $\psi_p - \psi_{FS}$ represent the potential on the polymer chains and in the solution within the fiber (assumed uniform) respectively, the dissociation of a group within the fiber involves the hydrogen ion in an initial change of potential of $(\psi_p - \psi_{FS})$. The intrinsic acid dissociation constant is

$$K_0^1 = \left(\frac{\alpha}{1-\alpha}\right) a_{H_1} \exp\left[(\psi_p - \psi_{FS})\frac{F}{RT}\right] \tag{1}$$

where α is the degree of dissociation, a_{H_1} is the hydrogen ion activity in the sorbed solution, and F is the Faraday.

For equilibrium between the fiber and the external solution, the Gibbs–Donnan equations hold:

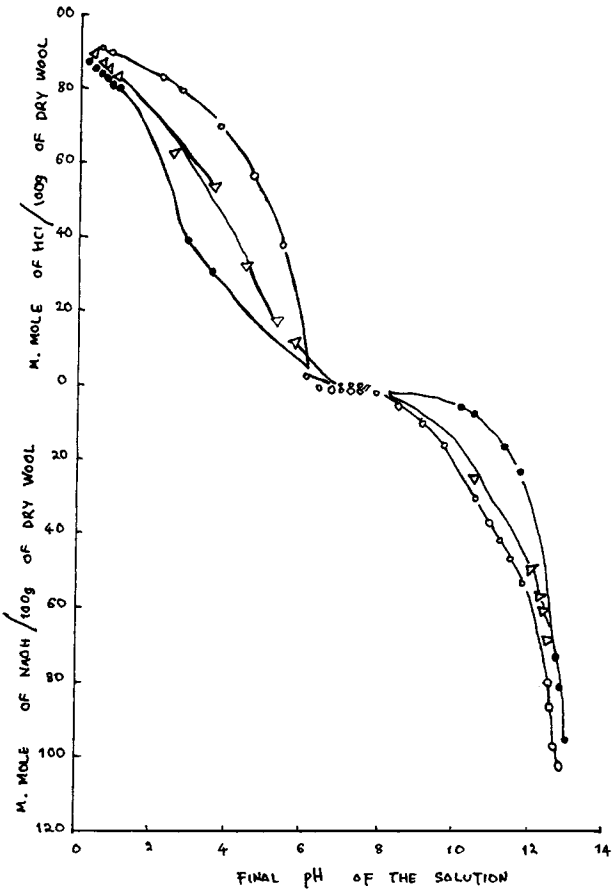

Fig. 4. Acid–base titration of Yankasa wool at 25°C: (⊙) no salt added; (X) 0.1 *M* NaCl; (⊡) 1.0 *M* NaCl.

$$RT \ln \frac{a_{H_1} a_{M_2}}{a_{H_2} a_{M_1}} = -\pi(\overline{V}_H - \overline{V}_M) - (\Delta\mu_H^0 - \Delta\mu_M^0) \tag{2}$$

where M is the univalent metallic cation (if present); subscripts 1 and 2 refer to the fiber and external solution phases; and π, $\overline{V}$, and $\Delta\mu^0$ are osmotic pressure, partial molar volume, and change of standard chemical potential between the fiber and the external solution, respectively. It is assumed that only a single simple anion is present and that $\overline{V}$ is independent of pressure. Combination of these equation gives an equation for the pH of the external solution:

$$\mathrm{pH}_2 = \mathrm{p}K_0^1 - \log \frac{1-\alpha}{\alpha} + \log \frac{a_{M_1}}{a_{M_2}} + \frac{0.4343}{RT} \times [(\psi_p - \psi_{FS})F - \pi(\overline{V}_H - \overline{V}_M) + \Delta\mu_M^0 - \Delta\mu_H^0] \tag{3}$$

For fibers with little swelling, it is reasonable to assume that the small amount of sorbed solution is at the same potential as the polymer chains of the fiber, i.e., that $\psi_p = \psi_{FS}$. Further, since the potential of the external solution is zero, it follows that

TABLE II
Carboxyl Dissociation Constants

Wool	pK_p^1	pK_q^1
Merino at 25°C	4.80	2.36
Crossbred at 25°C	4.80	2.54
Yankasa at 25°C	5.20	2.40
Lincoln at 0°C	4.85	3.58

$$\log \frac{a_{M_1}}{a_{M_2}} = \frac{0.4343}{RT}(-\psi_p F - \pi \bar{V}_M - \Delta\mu_M^0) \tag{4}$$

Equation (3) then reduces to

$$pH_2 = pK_0^1 - \log \frac{1-\alpha}{\alpha} - \frac{0.4343}{RT}(\psi_p F + \pi \bar{V}_M - \Delta\mu_H^0) \tag{5}$$

It is reasonable for these systems to regard $\Delta\mu_H^0$ as zero unless the anion has a powerful affinity for the fiber in its own right, as occurs with acid dyes, for example. Also, information on π has been obtained from studies of water absorption, and the term $\pi \bar{V}_H$ has been shown to be negligible.[8]

So far, on ampholyte fiber with little swelling and in the presence of an anion with no specific affinity for it, the pH of the external solution in equilibrium with it may be represented as

$$pH_2 = pK_0^1 - \log \frac{1-\alpha}{\alpha} - \frac{0.4343}{RT}\psi_p F \tag{6}$$

If ψ_p can be calculated, pK_0^1 can be found. The simplest assumption is that of a uniform potential distribution,[8] leading to

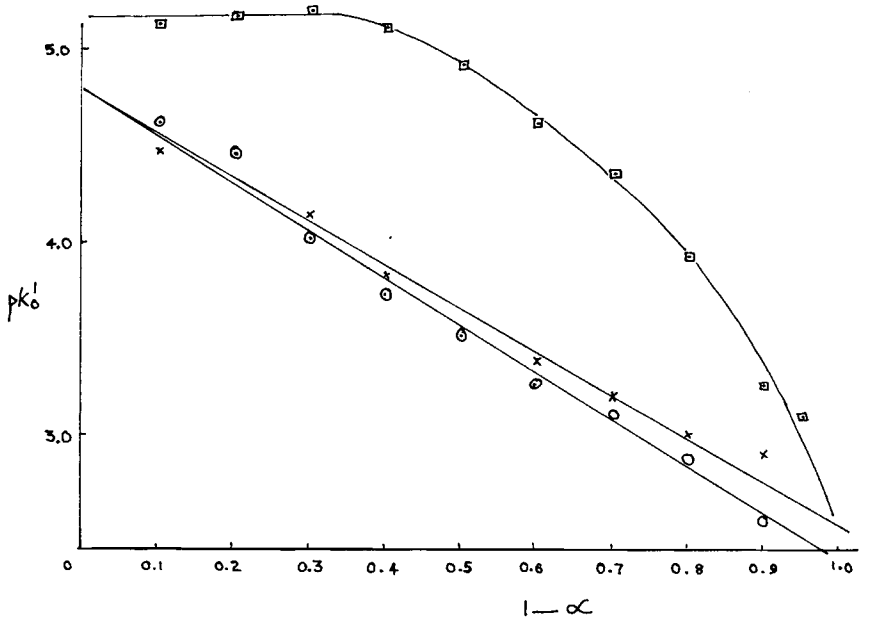

Fig. 5. Variation of intrensic dissociation constant pK_0^1 of the carboxyl groups with degree of dissociation: (⊙) Merino; (X) crossbred; (⊡) Yankasa.

$$\psi_D \frac{F}{RT} = \sinh^{-1} \frac{C_F}{2C_S} \tag{7}$$

where C_F is the concentration of net positive fixed charges on the polymer chains and C_S is the electrolyte concentration in the external solution. Equations (6) and (7) were successfully used by Mathieson and Whewell[8] to interpret the acid titrations of nylon[12] and Lincoln wool.[8]

Application of the Theory to Present Results

Using eqs. (6) and (7), values of pK_0^1 have been calculated for different values of α, together with swelling results,[1] to enable C_F to be calculated, and the results are shown in Table II. Within experimental error, pK_0^1 is independent of ionic strength but varies with α as shown in Figure 5. For Merino and crossbred wools, this variation is linear:

$$pK_0^1 = 4.80 - 2.44(1 - \alpha) \text{ (Merino)} \tag{8}$$

$$pK_0^1 = 4.8 - 2.54(1 - \alpha) \text{ (crossbred)} \tag{9}$$

For Yanakasa wool, however, the result is different, the pK_0^1 value remaining approximately constant for $1 - \alpha = 0$–0.4, at $pK_0^1 = 5.2$; thereafter, it falls non-linearly to 2.4 at $1 - \alpha = 1.0$.

The behavior of Merino and crossbred wools is similar to that reported earlier for Lincoln wool[8] at 0°C. This was interpreted as being due to the presence of two kinds of carboxyl dissociations: one with a high pK_0^1 the normal one, and the other with a low pK_0^1 due to salt linking to a charged basic group, and present in approximately equal proportions.[8] The expression for Lincoln wool at 0°C was

$$pK_0^1 = 4.85 - 1.27(1 - \alpha) \tag{10}$$

The values of the two carboxyl dissociations are obtained at $1 - \alpha = 0$ and $1 - \alpha = 1$ and were labeled pK_p^1 and pK_q^1, respectively. The values for Lincoln, Merino, and crossbred wools are shown in Table II.

The dissociation constants for the normal carboxyl groups are essentially the same for Merino, crossbred, and Lincoln wools and call for no comment. For Merino and crossbred wools, however, the salt-linked groups have a much lower pK_q^1 than for Lincoln wool, implying that the salt link is stronger in these two wools. There is little difference between Merino and crossbred wools in their carboxyl dissociations.

Yankasa wool behaves differently. The pK_0^1 value $1 - \alpha = 0$ is higher than the normal value for carboxyl groups in wool and is closer to the value found in nylon,[12] while the value for $1 - \alpha = 1$ is similar to those for Merino and crossbred wools, indicating salt linking for some groups. The shape of the curve would suggest that only the "normal" groups titrated up to $1 - \alpha = 0.4$; thereafter both groups titrate, but they are not present in equal proportions. However, the behavior of Yankasa is so different from that of the other wools studied that some entirely different explantion may be in order. For example, Yankasa wool is heavily medullated,[1] and if it is penetrated by aqueous medium, the calculations made may not be valid.

TABLE III
Dyeing of Merino and Crossbred Wools at 70°C

Dye	Merino wool		Crossbred wool	
	Time for 50% exhaustion, min	Maximum % exhaustion	Time for 50% exhaustion, min	Maximum % exhaustion
Naphthalene Black				
pH 2.0	3	100	4	100
pH 4.0	18	99	24	99
Orange II				
pH 2.0	2	98	3	93
Bismarck Brown				
pH 4.0	6	95	22	93
pH 9.5	—	14	—	25
Crystal Violet				
pH 9.5	1	98	1	98

The Alkali Titration

Here, there is little difference between the titration curves for the three wools. Histidine, lysine, and terminal amino groups titrate first, followed by arginine, tyrosine, and hydrolysis products. Some evidence may have been found for Merino wool of a plateau in the titration curves around 110–120 mmol NaOH per 100 g wool, but there is little sign of this for the other two wools.

Dyeing Properties of the Wools

The acid–base properties of Merino and crossbred wools are very similar, and this, combined with their similarity in mechanical properties,[1] suggests that the dyeing properties of the two wools should also be similar. That this is indeed the case is illustrated in Tables III and IV where the time for 50% exhaustion of the dyebath and the maximum % exhaustion are shown for the two acid dyes Naphthalene Black and Orange II and the two basic dyes Bismarck Brown and Crystal Violet. Like the mechanical properties,[1] the dyeing properties of the crossbred wool are only slightly inferior to those of Merino, confirming the conclusion already reached[1] that the crossbred wool could be used for the same wide range of textile applications for which Merino wool is famous, while the

TABLE IV
Time of Half-Dyeing and Percentage Exhaustion at Different Temperatures[a]

Temperature, °C	Merino wool		Crossbred wool		Yankasa wool	
	Time for 50% exhaustion, min	Maximum % exhaustion	Time for 50% exhaustion, min	Maximum % exhaustion	Time for 50% exhaustion, min	Maximum % exhaustion
25	18	59	21	60	80	11
40	10	75	13	70	78	15
60	6	94	9	77	71	19
70	2	98	3	92	45	20

[a] Acid dye: Orange II at pH 2.0.

crossbred sheep thrive much better under Nigerian conditions.[5] The Yankasa wool, due to a large proportion of medulla, behaves differently[13] in that it is very difficult to dye. Further investigations on dyeing properties of Yankasa are under progress.[13]

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