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Scanning electron microscope studies of the grain surface of leather

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The scanning electron microscope showed that the grain surface of leather (i.e. the surface exposed when the epidermis is removed in manufacture) was covered with a layer of non-fibrous material which was more resistant to rubbing in chrome-tanned ox hide than in chrome calf leather. Rubbing burnished the chrome-tanned ox coating which then, apart from occasional line cracks, appeared featureless, but in chrome calf the coating first broke into crenellated plates of fairly uniform size. The coating appeared to be a single layer but the plates could ride over each other during rubbing, to simulate a multi-layered structure. Although the under surface of the cover looked non-fibrous, some appearances suggest that it surrounded fine surface fibres and, when the coating was removed by rubbing, these fibres went with it. The cover was not extraneously produced during processing. It was resistant to the conditions of manufacture of the skin into leather, which included extremes of pH (pH 12.5 to 2.0), the use of a reducing agent (sodium sulphide) and brief treatment with a crude tryptic-type enzyme. It was also resistant to acetone and to dichloromethane.

Experimental processing was, at best, only partially successful in producing a grain surface clear of the coating.

1. Introduction

The three-dimensional fibrous weave of the animal dermis makes it extraordinarily versatile for making a great diversity of leathers. Some leather properties relate to the type of animal skin used: for instance sheep skin is small, lightweight, thin and soft, while ox hide is large, thick, heavy and firm*. But from any one type of skin the tanner by appropriate processing can make a wide range of leathers fitted for a variety of applications and often requiring opposing properties. For example, sole leather ranges from firm to flexible and from thin to stout: shoe upper leather ranges from firm to soft; it must conform to the foot, yet retain good shape; it should resist water penetration yet absorb moisture from the foot and transmit water vapour.

Fig. 1 illustrates diagrammatically the structure of skin [1] as seen in cross-section under the light microscope (LM). In life the dermis, consisting mainly of collagen fibres, is covered by the epidermis, the inner layers of which are living cells while the outer layers have become keratinized. Hair follicles pass through the outer layer of the dermis and are surrounded by fine fibres which gradually merge into the coarser fibres of the inner layer, the corium major. At the innermost side (the "flesh" side) the fibres lie parallel to the surface, so forming a limiting layer appearing horizontal in cross-section.

The hair and epidermis are removed by the tanner with an aqueous mixture of lime and sodium sulphide, and the surface so exposed becomes the grain of the leather. The skins may be immersed in the so-called "lime liquor" or they may be painted on the flesh side with a paste of lime and sulphide and then immersed in the lime liquor, the pH of which may be as high as 12.5. The pH of the unhaired skin – i.e. the pelt – is lowered (the pelt is "delimed") to 8-9 by, for example, ammonium sulphate, in preparation for bating which is an enzyme treatment utilizing crude tryptic-type enzymes. The precise function of bating is not understood but it makes the pelt soft and silky and seems to clean the grain. The pH is thereafter further lowered by acid, with salt present to prevent

*To the tanner "hide" is thick skin: in this paper the general use of the word "skin" is not intended to exclude hide.

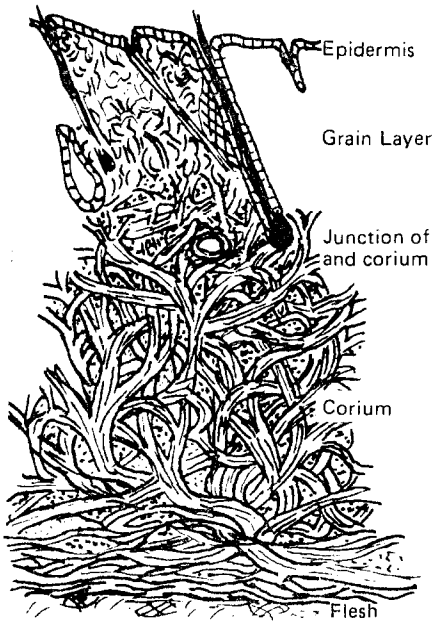

Figure 1 Diagram of cross-section of ox hide.

undue swelling of the collagen – a pickling process in which the pelt may be brought as low as pH 2. Immersion in tanning solution follows and penetration and fixation of the tan are controlled by pH, temperature and concentration. After tanning the leather is usually dyed. If dried without lubrication the fibres would adhere to each other and thus cause the leather to be harsh and inflexible. Grease, e.g. sulphated fish oil, is, therefore, applied to the wet leather in the form of an emulsion in water (the fatliquor), and drying brings it to the "crust" state. To make the leather feel mellow various mechanical treatments follow, for example, staking – the application of numerous small flexing movements. Finally, finishes, which may be protein, nitrocellulose or polymer, may be applied to the grain according to current demand. Prior to this application the leather is said to be "unfinished".

Leather is thus a three-dimensional meshwork of modified collagen fibres and its physical properties depend essentially on the individual fibres and their ability to move over each other. Both these aspects are affected by the conditions of manufacture. Natural collagen absorbs water at high and low pH values so that the fibres swell, shorten and twist. Under some conditions of processing the fibres will split longitudinally into more slender fibres and fibrils, necessary in the production of flexible leathers: under other conditions they will restick to give coarse fibres or, in the extreme, a solid inflexible structure. Hence, not only is the appearance of the fibres and their interweaving a key to the properties of a particular leather, it also reveals information about the processing through which the leather passed, and often offers an explanation for a defect which cannot otherwise be easily traced.

The bulk of leather microscopy has so far been done with the LM [1, 2]. This, however, does not resolve the very fine structure of the grain surface, either in section or in surface view, and it was hoped that the scanning electron microscope (SEM) would prove a means of investigating it further. Stirtz [3] in a transmitting electron microscope (EM) study by section and replica showed the presence just below the dermo-epidermal junction of extremely fine, non-collagenous fibres, and in leather a partial covering of non-collagenous material. The present investigation has not established a relationship between the appearance of the surface structure and physical properties of the grain but some new features of the grain surface have been observed.

2. Experiments and observations

2.1. Preparation of specimens

For surface examination, specimens about 2 mm × 7 mm were aligned on stubs with hair follicles opening towards the north of the stub as viewed under the microscope. For examination in section, 1 mm thick crosscuts were made with a hand microtome, but this proved inadequate for revealing the extreme grain surface and more sophisticated EM sectioning methods need to be tried.

Specimens were mounted on stubs with double-sided adhesive tape, and double-coated with evaporated layers of carbon and gold palladium, each with a nominal thickness of 20 nm. They were examined in a Cambridge Stereoscan 11A operated at an accelerating voltage of 10 kV. The specimens were tilted 45° to the electron beam.

Wet material was, at first, freeze dried for examination but in later work the simpler method of dehydration in acetone was found to be satisfactory. Specimens that required degreasing (as for instance, at later stages in leather manufacture) were extracted with dichloromethane after treatment with acetone.

2.2. Surface appearance

The finish was rubbed off the grain of a leather

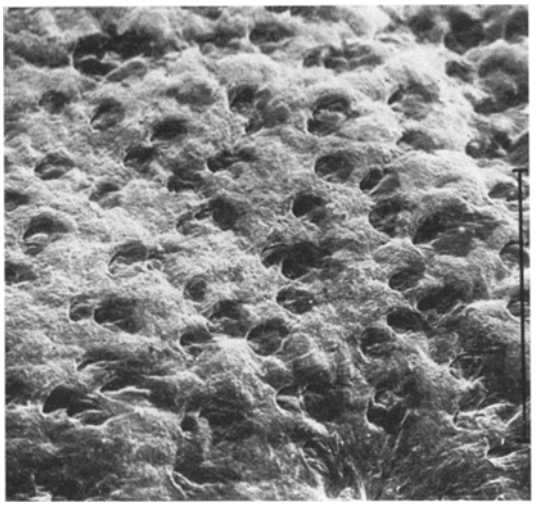

Figure 2 Grain surface of an ox hide leather. (Scale bar, 1 mm.)

by hand with cotton wool wet with 10% ammonia, and Fig. 2 shows its general appearance. The tissue between hair follicles was seen (Fig. 3) as a complex of fibres coming up from the interior and running a short distance in the surface before returning to the interior. The fibres occurred singly and as bundles and were sometimes arranged to form pores. However, when calf skin and ox hide were examined at various stages in manufacture (limed, bated, pickled, tanned, dyed and fatliquored, and dried), a coating was seen to be present at each stage with evidence of some patchiness. The coating is illustrated in Figs. 4 and 5 of calf after fatliquoring. It appeared non-fibrous and showed numerous pores.

2.3. Rubbing tests

With the possibility in mind that in the preliminary examination the coating may have been removed when the finish was being rubbed away, unfinished calf and ox leather were rubbed by three different testing machines used for leather.

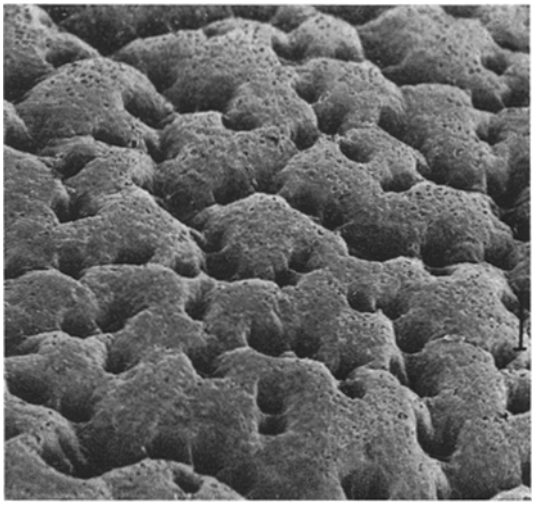

Figure 4 Fatliquored chrome calf. Note cover and pores. (Scale bar, 100 μm.)

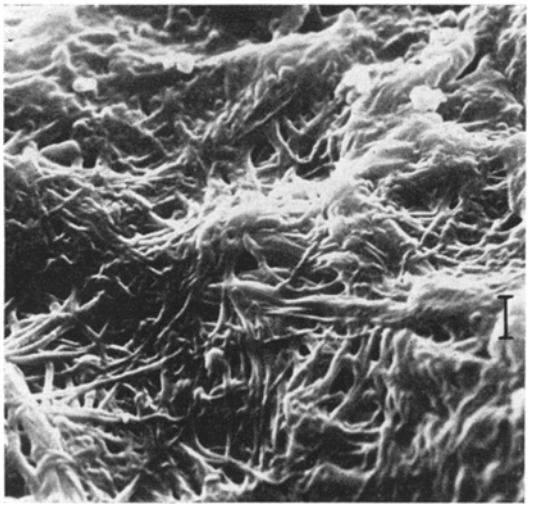

Figure 3 As Fig. 2, showing fibrous tissue between follicles. A pore is at the centre. (Scale bar, 1 μm.)

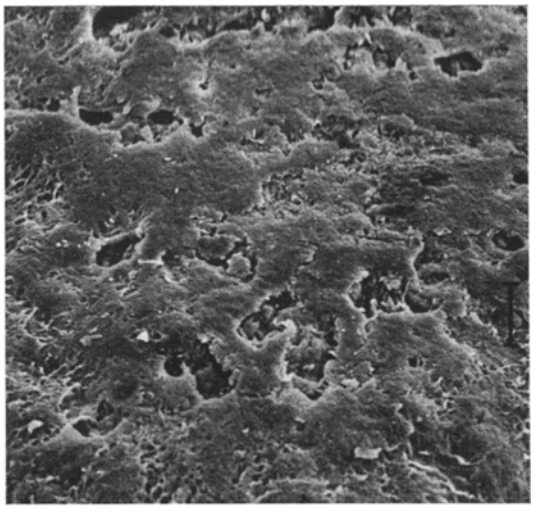

Figure 5 As Fig. 4, showing non-fibrous nature of the cover. (Scale bar, 10 μm.)

2.3.1. The crockmeter [4]

A square rubbing foot 2.5 × 2.5 cm², moves back and forth over the surface being tested, under 75 g load, along a 15 cm path at the rate of 500 strokes per hour. To simulate the earlier conditions the leather was wetted with 10% ammonia and the foot was covered with a close-weave cotton cloth.

2.3.2. The Martindale abrasion machine [5]

The circular test piece, 2.5 cm in diameter, is clamped to a foot which, under 700 g load, moves horizontally in a Lissajous figure against a 10 × 10 cm² of coarse cross-bred wool fabric: the foot completes 200 cycles per hour. The leather was rubbed in the dry state.

2.3.3. The Veslic rub-fastness tester (Swiss Leather Chemists' Association)

A square of wool felt, 1 cm across, is rubbed under 1 kg load along a 4.5 cm path over the surface being tested at the rate of 40 strokes per min. In principle, it is the same as the crockmeter with, in addition, a facility for stretching the test sample in a direction parallel to the direction of rubbing. The leather was stretched 20% and rubbed with a dry pad.

The three machines had similar effects on the cover and none succeeded in clearing it away without also removing some of the underlying dermal fibres. No fine effects related to the amount of rubbing were recognized, and the illustrations have been chosen to demonstrate characteristics of the coating.

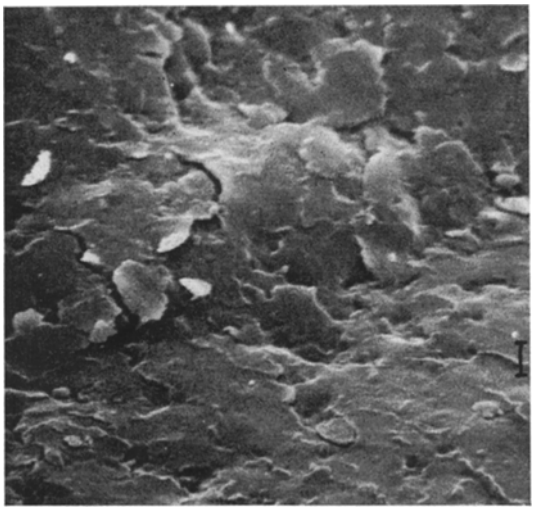

Figure 6 Calf cover breaking under rubbing into notched plate-like segments. (Scale bar, 1 μm.)

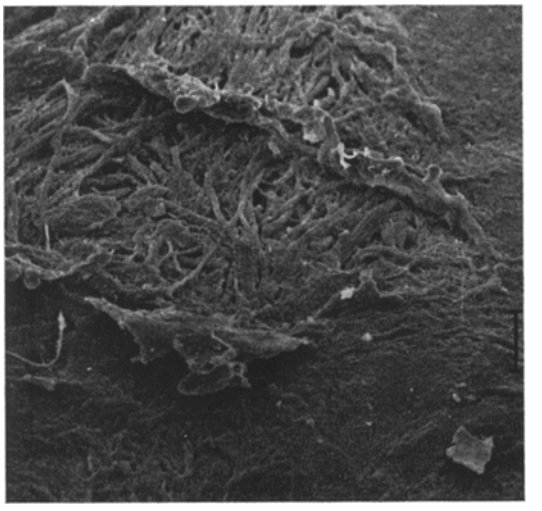

Figure 7 Rubbed calf cover turned back to expose dermal fibres: it appears single-layered. (Scale bar, 10 μm.)

The coating over ox hide leather burnished as a result of rubbing and, apart from occasional line cracks, appeared featureless. Where calf was burnished the surface showed small rounded knobs, presumably related to wrinkles sometimes seen (see below) in underlying fibres. After that, at an early stage in rubbing, the calf coating appeared to break into plates of a fairly uniform size, with crenellated edges. Fig. 6 shows some broken coating, and some not yet broken but with notched outlines apparent. In Fig. 7 the broken coating is shown turned back and single-layered: fine fibres stretch between the exposed dermal fibres which (although from the younger animal) appear coarser than the surface fibres shown in Fig. 3 and to form bundles. Perhaps the surface fibres were rubbed away with the coating, perhaps they were immersed in the coating. Although the under surface of the coating does not appear fibrous in Fig. 7, the possibility of immersion is supported by Fig. 8 where surface-size fibres appear to emerge from within the breached coating material. Sometimes the coating appeared to be broken into strips, sometimes it rolled, and sometimes the plates seem to have ridden over one another to give a multi-layered effect (Fig. 9).

2.4. The effect of processing

To study the origin of the coating, ox and calf

skin were experimentally unhaired. One possibility is that it derives from the basal membrane of complex structure which has been observed in EM studies between the dermis and the epidermis [6]: according to Dodson [7], when the epidermis is separated from the dermis the membrane may remain with either part, depending on the separating agent, but its attachment to the epidermis is stronger than to the dermis. A second possibility is that it consists of residues of the basal epidermal cells.

The outer layers of the epidermis and the hair from about two-thirds up its length within the grain layer, are keratinized and, therefore, subject to attack by sulphide under alkaline conditions [8]. Immersion in a suspension of lime alone (a "white lime") slowly removes epidermis and the entire hair root, the first action of the lime on the epidermis and follicle wall being the alkaline disintegration of the basal, non-keratinized layers [9]. Immersion in a lime liquor containing sodium sulphide allows a rapid attack on epidermis and hair to proceed from the keratinized exterior. When a lime-sulphide paint is applied to the flesh side it diffuses through the skin and, just below the grain surface, attacks the hair shaft where it is already keratinized, while basal layers of the epidermis tend to resist [10]. The hair roots commonly remain in leather and are large enough to see at low magnification, but, if a residue of non-keratinized epidermis remains, it is unresolved by LM.

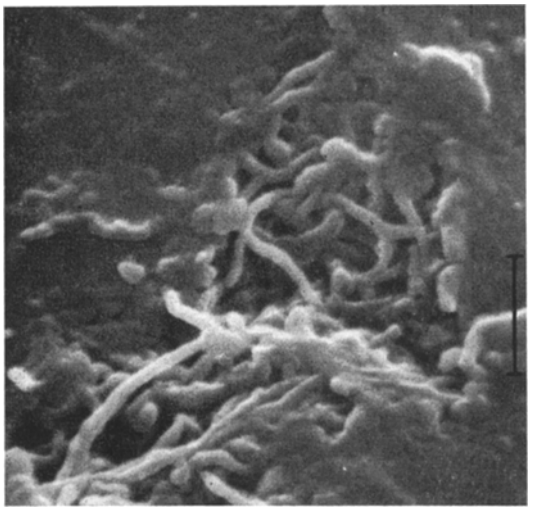

Figure 8 Fibres emerging from rubbed cover. (Scale bar, 1 μm.)

An attempt was made to provide a rapid sulphide attack on the hair simultaneously with, but distinct from, the alkaline attack at the dermo-epidermal junction. With meagre water, a paint will not fully penetrate, so a dryish lime-sulphide was painted on the flesh side of calf and ox skin. After some hours the residue of paint was hosed away and the skins were immersed in white lime with the idea that this would carry the sulphide in further to attack the sub-surface hair shaft and at the same time the epidermis

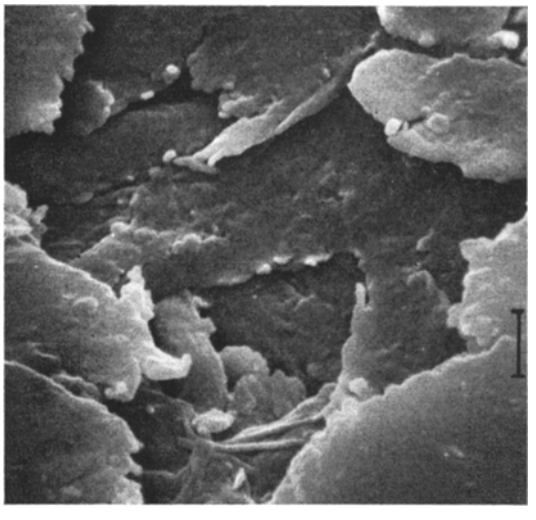

Figure 9 Segments of cover rubbed over one another to give a multi-layered effect. (Scale bar, 1 μm.)

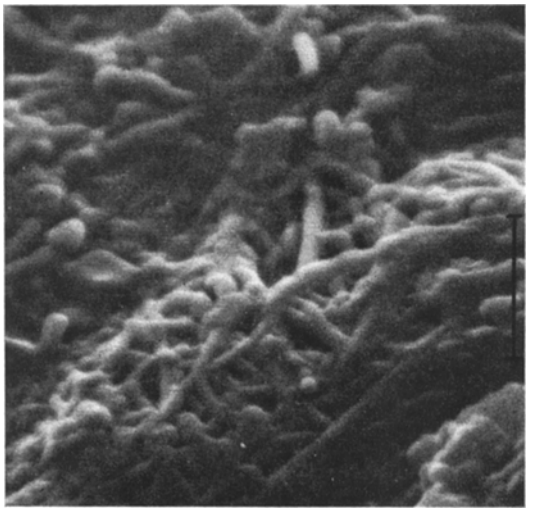

Figure 10 Fibrous appearance of the grain surface of experimentally unhaired pickled calf skin. (Scale bar, 1 μm.)

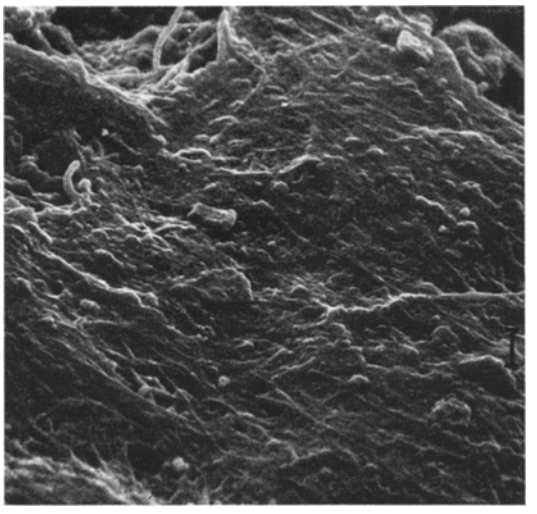

Figure 11 Calf skin of Fig. 10 after fatliquoring. A thin cover is apparent over the fibres. (Scale bar, 1 μm.)

could be attacked both externally and internally by the alkalinity of the treatment. Some ox hide was also unhaired by white lime. These attempts were, at best, only partially successful. Fig. 10 shows the pickled calf skin with clean fibrous surface, but at other stages the surface was coated and Fig. 11 shows the fatliquored stage with the underlying fibrous structure thinly covered.

3. Discussion and conclusions

The studies reported herein were undertaken on the assumption that the grain surface of leather is fibrous and that the appearance of the fibres under SEM would relate to their properties and the processing through which they had passed. Such a relationship has already established the profitable role of low magnification LM in studying leather. However, the assumption proved mistaken. A single-layered cover was found which, although slightly patchy, effectively prevented examination of the underlying fibres. Hand-cut preparations proved inadequate for studying the coating in section and further work on this aspect is envisaged.

The coating appeared non-fibrous and was more robust in ox hide leather than in calf. Its origin and nature were not revealed in the investigation. The coating was present over the leathers before they were rubbed and, hence, was not produced by the method of preparing the specimens for examination. Two observations indicate strongly that it was not merely deposited from an external source under conditions of processing. The pores shown in Fig. 4 were presumably related to such as that shown in Fig. 3, which, it may be assumed, were the channels through which nerve endings passed from the dermis to the epidermis during life. Secondly, the segments into which the cover broke on rubbing were of characteristic shape (Fig. 6) and were able to ride over one another (Fig. 9). The surface viewed was that towards the epidermis (removed early in processing) and the outlines of the plate-like segments suggest a relationship between them and the epidermal cells. Evidence is lacking as to whether the coating arose from the basement membrane between dermis and epidermis or formed from degradation of basal epidermal cells. Patchy removal of the coating occurred during manufacture. The reason for the patchiness is not clear: it would seem reasonable, though experiments did not unambiguously confirm it, that it was associated with the method of removing hair and epidermis. The coating was so closely interlocked with the outer dermal fibres that rubbing did not remove it unless it also took dermal fibres with it.

The coating was resistant to conditions of manufacture including immersion in liquors of high to low pH (pH 12.5 to 2.0), use of the reducing agent sodium sulphide, and brief subjection to crude enzyme of mainly the tryptic type. It was also resistant to acetone and to dichloromethane which were used to dehydrate and degrease specimens for examination.

The non-fibrous nature of the coating indicates that the cover does not contribute to the flexural strength of the grain. It possesses some toughness, greater in ox than in calf, but precisely how it affects such properties as brightness of grain and scuff resistance remains to be determined.

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