



Figure 1: Cross-section of finished leather with the surface coating visible.

Microscopical studies in leather manufacture

Part 4 of 4: Finishing

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The coatings produced in leather finishing are generally resin polymers or protein based applied using water as the medium. These finishes also contain other components such as pigments, dyes and matting agents to adjust the appearance of the leather.

Examination of the finish film cross-section

Finishes can be examined for film thickness or other routine purposes by binocular microscope using epi-illumination techniques. Sections are cut using a razor blade and the sections mounted on glass slides using double sided sellotape. The finish thickness is then ascertained by measuring it against a graduated eyepiece. This is calibrated against a stage micrometer and the coating thickness can then be calculated. This is important as the coating on leather must be below 0.15mm or it has to be termed as coated leather, and a section of finished leather examined under the light microscope is shown in *Figure 1*.

If more detail were needed, for instance, if the thickness of the different layers comprising the film were required, then the Scanning Electron Microscope (SEM) would be used. In this event, the cut section is stuck on an aluminium stub and gold coated prior to examination in the microscope. The thickness of the layers can thus be calculated against the marker bar. A cross-section of a finish film examined by SEM with

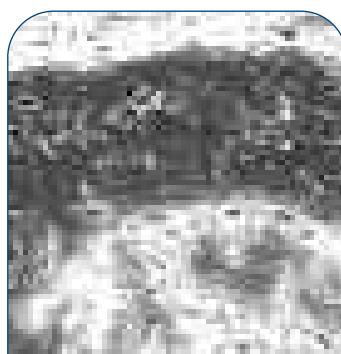


Figure 2: Cross-section of finished leather examined using the SEM. (Viewed at 1500x magnification).

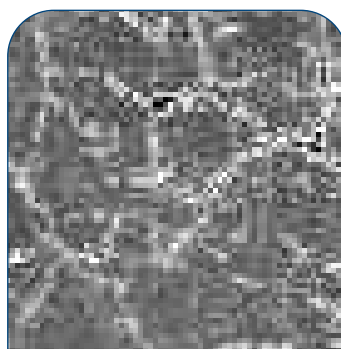


Figure 3: Upholstery leather exhibiting cracks in the surface coating. (Viewed at 250x magnification).

the different layers visible is shown as *Figure 2*.

Examination of both surface and cross-sections of coatings can also observe faults in the coherence of the finish film. If the test has to be non-destructive, the examination is restricted to the light microscope, however, if a more detailed examination is needed, then the SEM is used. Typical faults seen in finish films include cracking shown as *Figure 3*, air bubbles shown as *Figure 4*, and the presence of large particulate matter shown as *Figure 5*.

These faults lead to poor physical properties such as wet rub fastness and flexibility.

The cross-section of the finish can also be examined for faults in the coherence of the finish, such as large air bubbles as shown in *Figure 6*, and particulate matter.

Cracking of the finish can also be examined via the cross-section as it shows how far through the coating the cracks are penetrating and whether it is one layer or the whole finish which is failing.

SEM limitations, and alternative techniques

When examining finish films, the settings on the SEM must be carefully selected.

Many of the polymers used are sensitive to electron beam damage and crack under prolonged examination, with protein finishes being particularly susceptible.

In addition, when examining the surface of

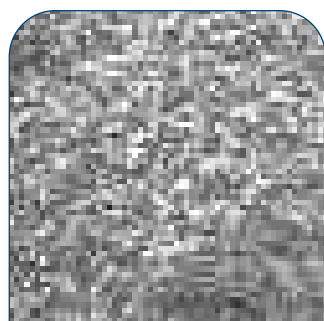


Figure 4: Small air bubbles visible in the surface coating. (Viewed at 250x magnification).

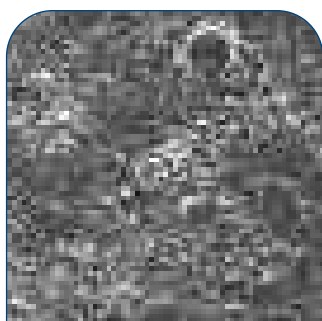


Figure 5: Large particulate matter in the top coat of the leather finish. (Viewed at 250x magnification).

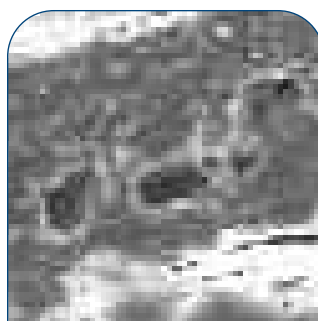


Figure 6: Cross-section of the finish of an upholstery leather showing air bubbles present in the film. (Viewed at 1000x magnification.)

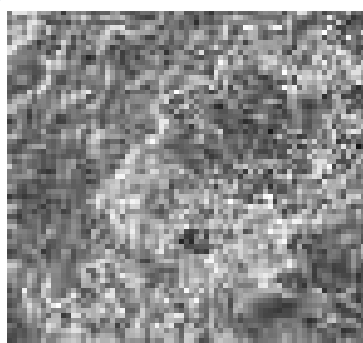
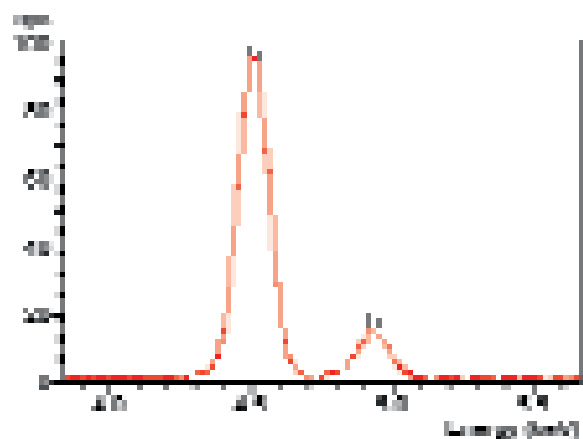


Figure 7a (left): Unknown surface deposit on finish.

Figure 7b (below): Unknown deposit identified as containing titanium by X-ray microanalysis.



the coating a high voltage can lead to a less detailed image, due to the electrons penetrating too far into the specimen. However, this sub-surface detail can be used as a problem solving tool using the back scattered electron (BSE) detector. The particulate nature of the underlying coatings can be seen using this technique, and has been used to show why apparently identical finished leathers had different physical properties.

X-ray microanalysis can be used to examine faults in finishes by carrying out elemental analysis of particulate matter on the surface or in the cross-section of the finish. An image of the specimen is acquired and the relevant particulate picked out for analysis. The spectra of the matter can then be compared to another more typical area to see if there are any differences. A typical example of this is shown in *Figures 7a* and *b* where the deposit on the surface of the finish when examined by X-ray microanalysis was shown to be titanium. As this was a

white deposit, the logical contaminant was titanium dioxide pigment.

Cryo-SEM is a technique which has been utilised to study aqueous based finishes^(Legend 1), following the leather industry's move away from solvent based polymers. Examination of both water and solvent based polymers can be carried out by placing small samples of liquid polymer between 2 rivets, then freezing in slushed liquid nitrogen. After freezing the rivets are separated and the

freeze fractured polymer surface examined. Detail of a fractured solvent based polyurethane resin is shown in *Figure 8*.

An alternative technique used to examine polymers using cryo-SEM involves splitting samples of leather down to approximately 0.3mm and then spraying them with an impermeable coating. When the coating is dry, a water based coating is sprayed onto the leather, instantly frozen to prevent the polymer drying, then fractured in the microscope. A freeze-fractured water based polyurethane resin as it begins to form a film on the leather surface is shown as *Figure 9*.

In this example the film formed by the polymer is more

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Light microscope uses in soiling investigations

In addition to studies relating to film formation, the light microscope has proved useful in soiling investigations, in particular the penetration of ink from pens through upholstery leather finish films. Polymer films dried to a uniform film thickness were subjected to various colours of ink applied to one surface of the polymer. The samples were then left for 24 hours at 20°C and 65%RH to see if there was any penetration of the ink into the polymer film. The samples sectioned to a thickness of 60µ and mounted on glass slides prior to examination revealed that inks penetrate into polymer films very quickly. Red ink ingressed more rapidly than either blue or black as shown by *Figures 10a* & *10b* (1).



Figure 10a: Polyurethane resin showing penetration of red ink after 24 hours at 20°C 65% RH.

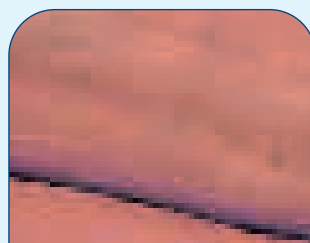


Figure 10b: Polyurethane resin showing penetration of blue ink after 24 hours at 20°C 65% RH.

This penetration into the polymer film was deeper than the thickness of a typical top coat, indicating the importance of studying soiling mechanisms to help develop graffiti proof finishes.

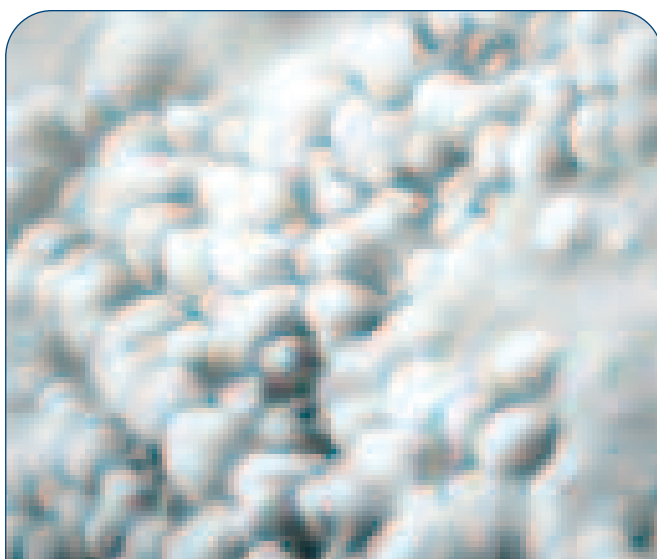


Figure 8: Freeze fractured surface of a solvent based polyurethane resin. (Viewed at 5000x magnification).



Figure 9: Water based polyurethane resin examined using Cryo-SEM to examine film formation. (Viewed at 9800x magnification).

particulate and less homogenous than that formed from the solvent based product. Microscopes are essential for examining all aspects of leather finishing from problem solving and defects through to studies on polymer films. 🌀

Legend

1. The settings which can be used when examining polymers by cryo-SEM are more flexible than those which can be selected in when using standard techniques as the polymers are less susceptible to heat damage from the electron beam.

References

Hudson, A., Langridge, D.A. & Obeso, I. 2002. Leather Finishing Soiling, BLC Journal, May, 88-91.