

A method to evaluate finished leather according to corrected or not corrected grain (FILK-QMA-1201)

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Abstract

The authors present a new method, which allows differentiation between finished leathers whose grain had been corrected or not corrected. The finish is removed completely from the leather surface, without destruction of either the leather surface or the finishing layer. This is possible by adhering the finish of the leather to a hard surface and removing the leather by treatment with solvent mixtures. The surface of the leather (grain side), the back side of the finish, as well as cross sections of the finished leather are evaluated by light microscopic and SEM investigation. In special cases it is reasonable to digest the leather component by enzymatic treatment to get a mirror image of the back side of the finish. The evaluation of all the images leads to the result “corrected” or “not corrected”. The method is fixed in the standard operation procedure FILK-QMA-1201.

Introduction

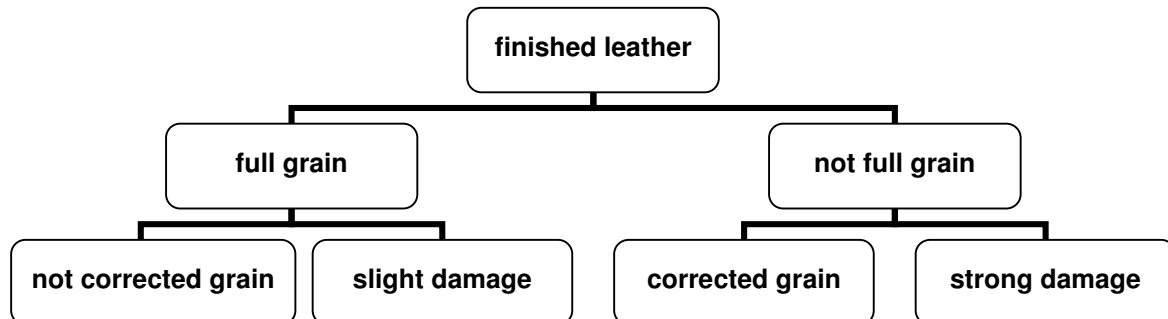
Up to now there was no reliable method, by which this correction / buffing of the surface could be verified. Usually the leather samples or the finish were treated with different solvents under careful rubbing to remove the finish from its substrate. The samples were then investigated by microscopic methods.

Because of the strong adhesion of the finish to the grain, especially of buffed leathers, it was often impossible to remove the finish without destruction of the surface of the leather. It was impossible to differentiate, whether the destruction of the surface was a result of the method or of the buffing treatment. Therefore, around one half of the assessments were uncertain when using this method.

This situation was unsatisfactory not only for the laboratories, which had to investigate the samples, but also for tanneries and their customers because of the loss of confidence. Therefore, the aim of our work was to find a method for a non-destructive removal of the finish from the grain, to get unambiguous results about corrections of the leather surface.

We will use the term “full grain” equivalent to “not corrected” leather. In our sense this leather could be finished or not. However, the natural porous structure of the grain has to be clearly visible after non-destructive removal of the finish if present. Slight damages of the leather surface or of the grain because of blemishes or mechanical stress during wet processes in leather manufacture are not interpreted as correction of the grain during assessment of the surface.

In contrast, we use the term “not full grain” for leathers where the grain had obviously been buffed (corrected) or where considerable damage to the grain can be observed, e.g. as a result of badly damaged raw material.



2 Method – FILK-QMA 1201

2.1 Principle

The surface and cross sections of the samples will be investigated by light microscopy and SE-microscopy. To investigate the finish the leather samples will be fixed with their grain side to a hard surface and removed from the leather. The backside of the finish is also used for the investigation. To get unambiguous results according to the standard operation procedure FILK-QMA-1201, an evaluation of all the different investigations is needed. This comprises the grain after removal of the finish, the backside of the finish of different preparation methods and the cross sections.

2.2 Sample preparation

Sample preparation is the most important step during the investigation. It is necessary to remove the finish from the surface without any damage of the grain. The removal is successful when no loosely bound leather fibres remain on the finish.

To remove the finish the leather is glued with the finished side onto a carrier with a flat hard surface according to EN ISO 11644 by the use of cyanoacrylate glue. After the fixing of the sample the leather is saturated with solvent from the flesh side. Suitable solvents are, e.g. mixtures of equal parts of 1 molar hydrochloric acid and methanol, formic acid and methanol or hydrochloric acid and acetone. Acetone often leads to a separation of the finishing layers among themselves. After penetration of the solvent the leather is slowly peeled away from the carrier. The time of beginning of the removal as well as the speed and the angle are dependent on the sample. This step also depends on the experience and the skill of the operator. After the removal of the leather, the samples have to be dried because fine structures of the surface are not visible from wet samples.

Often the base coat is of low viscosity when applied. Hence, it penetrates readily into the fibre structure of the surface, especially in regions with damages. In these cases the removal of the

finish by solvent is not easy and often leads to remainders on the grain surface, or the fibres are glued together. To overcome this the sample which is glued on the hard surface is soaked in a solution of 1% Alcalase 2.4 FG (Novozyme) at 50°C for several hours until the protein fraction has completely digested. The finish then remains like a mirror image of the grain surface.

To evaluate the cross sections the whole samples are cut without removal of the finish. It is important to include cross sections of the hair follicles.

Three samples in minimum are prepared from each leather to minimise the influences of local hide defects or variations in hide structure.

2.3 Microscopic analysis

The microscopic evaluation comprises: (i) assessment of the leather surface after removal of the finish, (ii) observation of the backside of the finish, (iii) observation of the backside of the finish after enzymatic digestion and (iv) investigation of the cross sections. To evaluate the samples a light microscope with high resolution is necessary or a scanning electron microscope (SEM). All pictures shown here are taken with a SEM Philips XL30 using the ESEM mode.

Before assessment of the samples their accurate preparation has to be controlled. The first step is to ensure that the finish has been removed completely from the grain. To check this, the surface is controlled by a microscope to examine whether there are any residues from the finish on the grain (Figure 1).

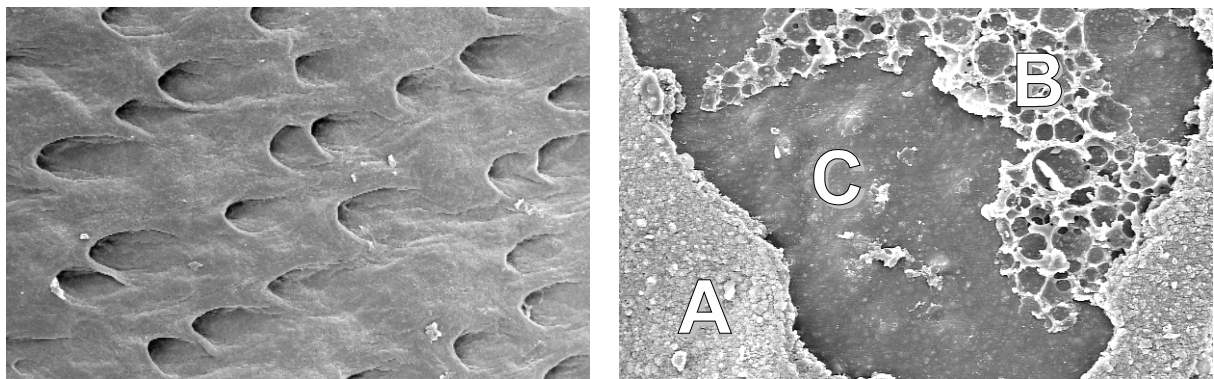


Figure 1: Leather surface after complete (left) and incomplete (right) removal of the finish layer; (A-original finish surface, B-foam layer, C-base coat) (viewed at 150x / 200x magnification)

In a second step it has to be verified that no leather fibres remained on the backside of the finish. If this is so one can see easily fibres or fibre bundles, which stick in the finish (Figure 2).

In both cases (pictures at the right side) the samples have to be discarded and new samples prepared.

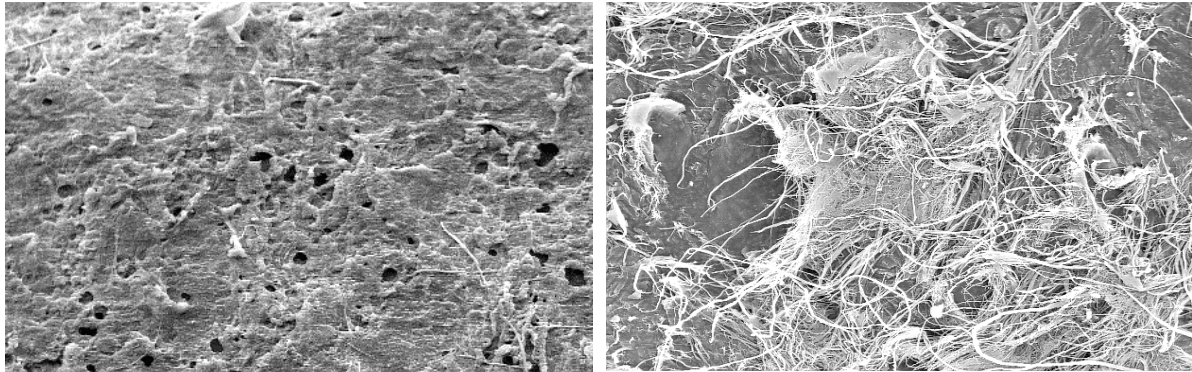


Figure 2: Back side of the finish layer after its removal from a corrected grain leather (left) without and (right) with remainders of fibres sticking in the finish. (viewed at 200x / 200x magnification)

On the basis of our experience it is not sufficient to investigate only the surface of the leather, the backside of the finish, or the cross sections alone, but it is necessary to assess all the pictures together.

2.4 Microscopic analysis of the grain

When surveying the surface of the leather the general appearance is assessed just as the status of the hair follicles.

Not corrected grain shows its fine structure. The openings of the hair follicles and especially the sickle shaped pellicles can be clearly observed and are without any damage (Figure 3).

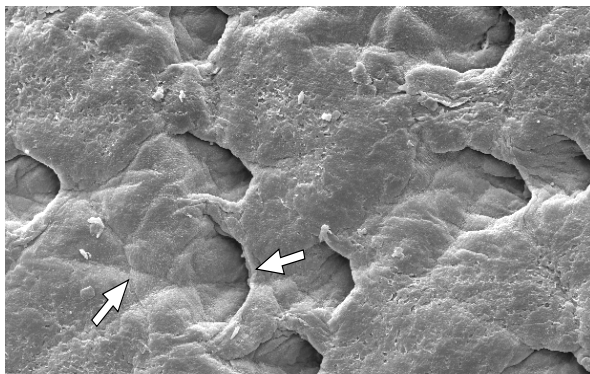


Figure 3: Leather surface of a full grain leather after successful removal of the finish. The sickle shaped pellicles and the fine structure are observed without any damage (arrows). (viewed at 200x magnification)

In contrast, if the surface had been buffed then the structure of the grain is damaged. Single leather fibres and fibre bundles can be observed. The openings of the hair follicles are damaged in varying intensities depending upon the intensity of the buffing treatment (Figures

4, 5 and 6). Usually the sickle shaped pellicles are strongly damaged. Often one can observe the fine structure of the grain or grind marks in deeper regions of the hair follicles.

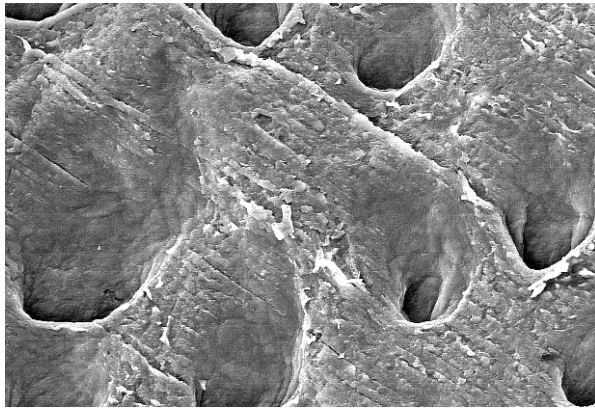


Figure 4: Surface of a slightly snuffed leather after removal of the finish. Parallel oriented grind marks are observed as a clear characteristic for correction. (viewed at 250x magnification)

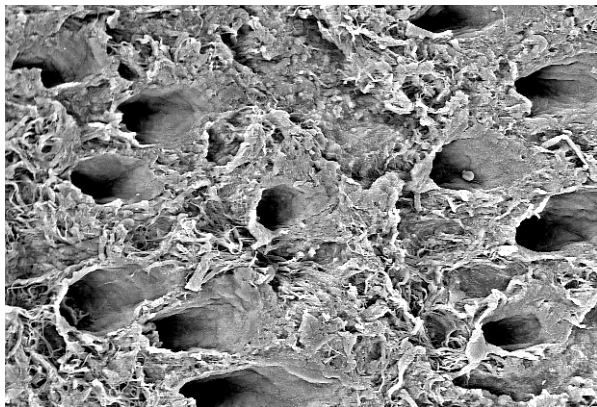


Figure 5: Surface of a buffed leather after removal of the finish. Truncated hair openings are observed as well as grind marks. (viewed at 200x magnification)

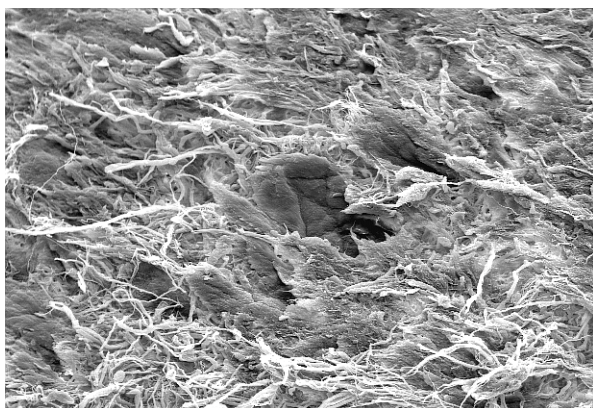


Figure 6: Surface of a strongly buffed leather after removal of the finish. Hair openings disappear in a surface looking like nubuck effect. (viewed at 200x magnification)

Other marks result from mechanical treatment of the leather surface, e.g. during brush dyeing. They look similar to grind marks but are only local and do not show the typical parallel appearance. Even when using very small grain size abrasive the marks are clearly observed. This was shown by experiments with buffing paper with a very fine grain size (1200), which were tested with crust leather (Figure 7).

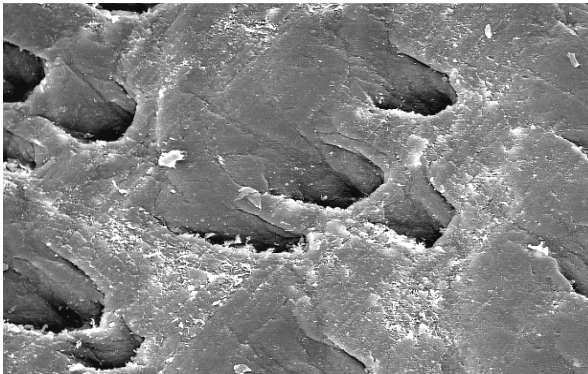


Figure 7: Surface of a crust leather after treatment with buffing paper (grain size 1200). Despite of the fine grain grind marks can be clearly observed. (viewed at 200x magnification)

2.5 Microscopic analysis of the back side of the finish

The microscopic assessment of the backside of the finish is a useful complement to the investigation of the grain. Often the fine structure of the grain appears better on the back side of the finish than on the grain itself (Figure 8). The finish which penetrated into the hair follicles is removed nearly completely by the sample preparation.

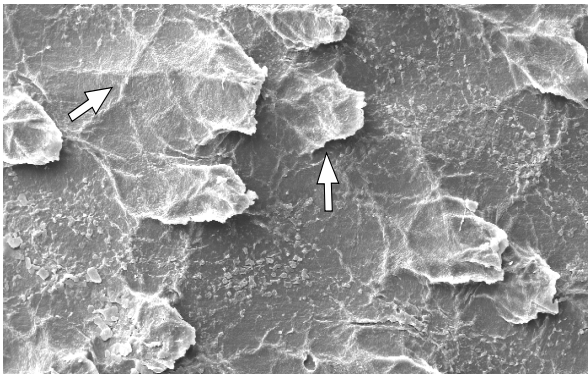


Figure 8: Back side of the finish from leather that was not corrected. The mirror image of the typical grain surface is clearly observed as a result of the base coat flowing into the hair openings. (viewed at 200x magnification)

Observing corrected leathers the hair follicles are usually scarcely visible. Rather, grind marks appear clearly (Figure 9) and also impressions of fibre bundles which lay on the surface of the leather and were agglutinated with finish material (Figure 10).

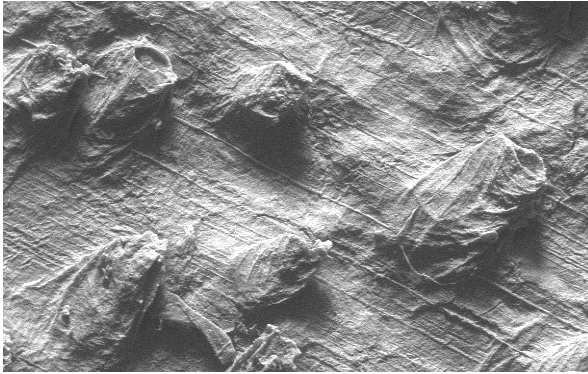


Figure 9: Back side of a finish of a leather that was slightly corrected. Grind marks are clearly observed. (viewed at 250x magnification)

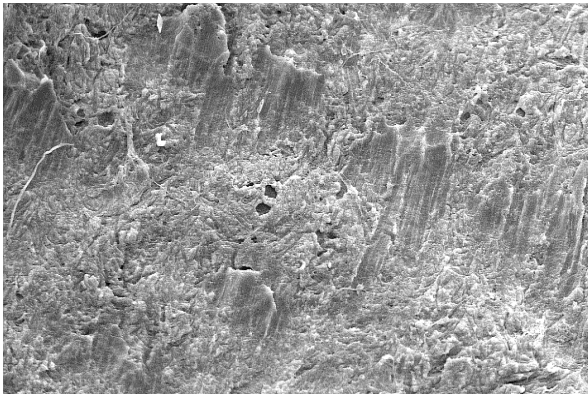


Figure 10: Back side of a finish of a corrected leather. Grind marks are clearly observed as well as the impression of leather fibres that were glued with the finish. (viewed 200x magnification)

In some cases, especially when the base coat had a low viscosity, the finish cannot be completely removed by the solvent described above. Then the leather substrate can be digested by enzymatic treatment. The back side of the finish remains like a mirror image of the leather surface. As can be seen in Figure 11 this leather had not only been buffed but also stuccoed. Both, the finish as well as the stuccoing mass are not removed by enzymatic digestion.

2.6 Microscopic analysis of cross sections

The microscopic investigation of the cross sections begins with the measurement of the whole thickness of the leather, the thickness of the grain and that of the finish. A thin grain and a thick finishing layer can be the first hints pointing at a corrected surface. However, the most

important criteria are the boundary layer between finish and grain and the opening of the hair follicles.

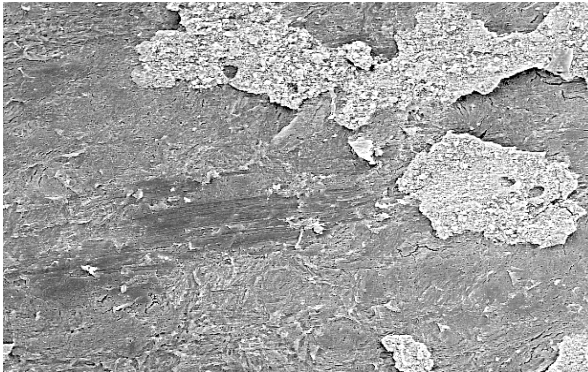


Figure 11: Back side of the finish of a leather that was stuccoed and corrected. The leather substrate was digested by enzymatic treatment. (viewed at 150x magnification)

Not corrected leathers show a clear boundary layer. Finish and grain can clearly be distinguished and the compact layer of the grain is not destroyed. Furthermore, the openings of the hair follicles show a complete curvature (Figure 12).

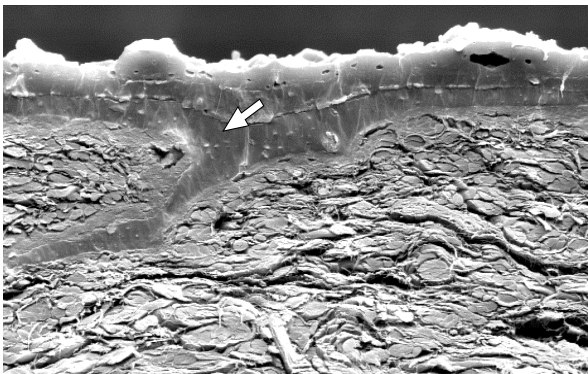


Figure 12: Cross section of leather that was not corrected. The curvature of the hair openings is completely preserved (arrow). (viewed at 1000x magnification)

If the leather is corrected the top of the grain is removed and often the finish has penetrated into the grain. The openings of the hair follicles do not show any curvature but a tapered hair channel as a result of the material loss during buffing (Figure 13).

If the grain had been damaged accidentally, e.g. by mechanical treatment during brushing, in some regions defects will be visible but in others no defects can be found. Furthermore, the curvatures of the openings of the hair follicles are usually found.

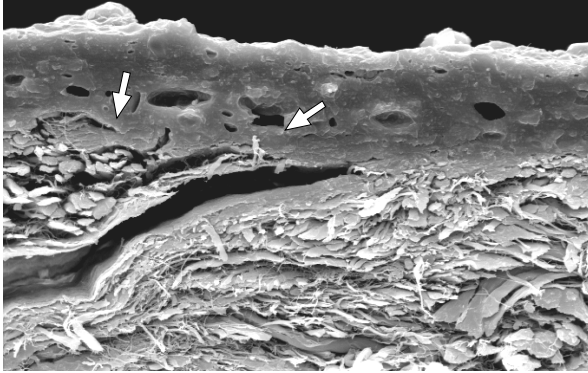


Figure 13: Cross section of a corrected leather. The curvature of the hair openings has been lost. They appear truncated, ending at the boundary layer in an acute angle. Base coat penetrated into the fibre network. (viewed at 1000x magnification)

3 Conclusions

This procedure of sample preparation and microscopic investigation has been found to be very sensitive in distinguishing between corrected and not corrected leathers. However, an important assumption for an accurate assessment is the complete removal of the finish from the grain. According to the standard operation procedure FILK-QMA-1201 by combining the information from the grain side as well as that from the backside and that of the cross sections together, it is possible to make a decision between “corrected” or “not corrected”.

Acknowledgements

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