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Formaldehyde and Acetaldehyde on Leather: Similarities and Discrepancies

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Abstract.

Formaldehyde and leather have a relation of over one hundred years, since formaldehyde is a very common building block for the synthesis of syntans and resins and has even been used for tanning as such. While there is a lot of literature and best practice around how to minimize formaldehyde in leathers on the basis of extraction methods, acetaldehyde is not used as a building block and rarely appears in extraction assays. However, it contributes to significant problems in emission test for automotive leathers, especially to meet the standards in the Chinese market. This article will reveal new emission data assembled by new measurements. A new, facile method will be introduced and exemplified with data across the process of leather making, from tanning to finished leather and across various chemistries applied.

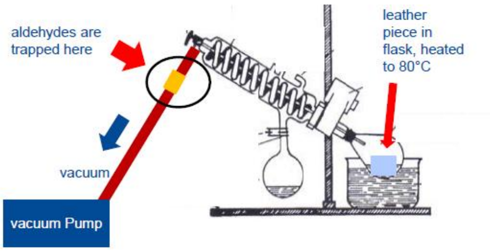
Keywords: Formaldehyde, acetaldehyde, emission, scavenging.

1. Introduction

While formaldehyde is a widely used building block for the synthesis of syntans and resins in leather (1), acetaldehyde is a natural product, not used in the process of leather making. While acetaldehyde has not created problems after extraction measurements of leather according to ISO 17226, it does appear in emission tests and the results created concerns (2), especially in automotive leather for the Chinese market, due to Chinese legislation: GB/T 27630-2012. So far, there are several emission chamber tests on the market, but the results are difficult to compare and only few data points about acetaldehyde emission can be created since the measurement takes several hours. We established a method for acetaldehyde emission suitable for screening to gain insights not only on finished leather, but also within the process of leather making and in order to compare the contribution of products.

2. Material and Methods

In VDA 275 aldehyde emission can be detected from water, stored on the bottom of a bottle with a piece of leather above the water. In these tests only a few ppm acetaldehyde are detected. In case of chamber emission measurements, the leather is conditioned in a closed chamber and the air is removed and analyzed for aldehydes. In these measurements significant values of acetaldehyde are detected. Automotive companies use these chambers to analyze volatile organic compounds either with raw material for the interior of cars, such as finished leather, textiles, or plastic, or with already assembled parts for the interior of cars. We developed a chamber on the basis of a rotation evaporator in which pieces of leather can be analyzed. The leather remains in the closed apparatus at 80°C water bath temperature and remains there for thirty minutes. Finally, the air is removed from the chamber via evaporation pump and aldehydes are derivatized to their dinitrophenyl hydrazones in a cartridge (3) positioned between the rotation evaporator and the pump, as shown in scheme 1. The hydrazone is washed off the cartridge and quantified via calibration curve on a HPLC.



Scheme 1. Acetaldehyde determination in a rotation evaporator

3. Results and Discussion

Initial measurements revealed that the acetaldehyde emissions are highest in the early stages of leather making like wet blue and are minimized on crust basis. It should be taken into account that the water content in wet blue is significantly higher than in crust. After finishing acetaldehyde emissions rise marginally, as can be seen in figure 1.

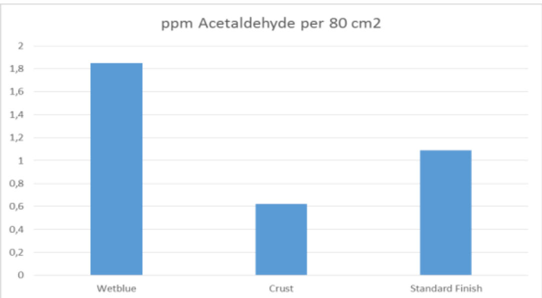


Figure 1. Acetaldehyde emission in three stages of the leather making process

These findings are similar within the wet white process. Although the boiling point of acetaldehyde is only twenty one degree Celsius the emissions from the leather do not minimize over time. In a long term study with finished leather the values of acetaldehyde emissions stayed the same in a period of ten month, as depicted in figure 2.

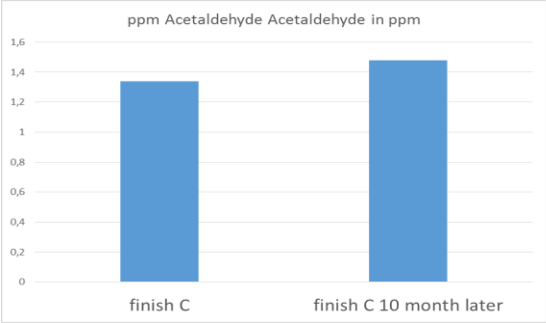


Figure 2. Acetaldehyde emission over time

Comparison of various wet end products like syntans, polymers, resins, or vegetable tannins did not reveal significant differences. This is why we focused on process modifications. In a study with three vacuum evaporations within the leather making process until crusting, about a 30% reduction of acetaldehyde emissions was achieved, compared to a leather made with only one evaporation after crusting. In this modified process, vacuum was applied once on wet blue, a second time in the middle of the wet end process between re-tanning and fat-liquoring and a third time after crusting. Results are shown in figure 3.

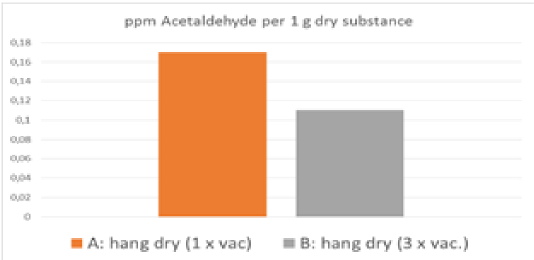


Figure 3. Reduced acetaldehyde emission after three evaporation, compared to one evaporation after crusting

The acetaldehyde emission were undertaken not directly after the vacuum on crust basis, but after a subsequent twelve hours hang drying in order to re-establish a comparable dry content. The dry content has a significant impact on acetaldehyde emission.

Scavenging substances for acetaldehyde were screened for emission reduction, but only few showed significant and reproducible results. As depicted in figure 4, a scavenger that was applied in a flesh side treatment via spraying on finished leather lead to a 30 % reduction of emissions.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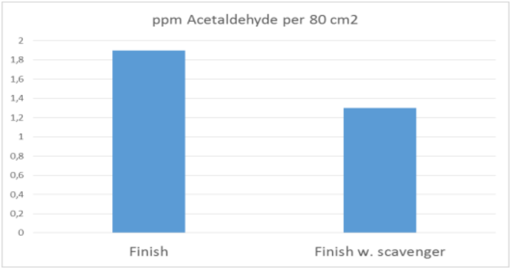

Figure 4. Reduced acetaldehyde emission after flesh side application of a scavenger via spraying compared to the untreated finished leather.

The same amount of scavenger applied in wet end did not lead to the same results, as achieved with flesh side application on finished leather.

Interestingly, acetaldehyde occurs in nature in the degradation of glucose and of threonine by microorganisms. However, while it is well possible that these microorganisms exist in the raw hide and produce acetaldehyde there, the possibility that these microorganisms survive the beam house and continue to function later stage in leather, is difficult to imagine.

4. Conclusion

We established a method to monitor the acetaldehyde emission within the process of leather making and on product basis by comparing different products on a one to one basis. While emissions are high in early stages, like wet blue, they are minimized on crust basis. After finishing acetaldehyde emissions rise marginally. Comparison of wet end products did not lead to significant reduction of emission. This is why we focused on process modifications. Applying vacuum three times in crusting compared to one time, lowered the emissions. However, this process modification adds complexity to the leather production process. Through application of a scavenger on the flesh side of finished leather, promising results were achieved.

While formaldehyde occurs in extraction analysis, if products with high formaldehyde content are used within the leather making process, acetaldehyde is not used as a building block, but appears in emission test. We managed to reduce acetaldehyde emissions via process modification and scavenging but the chemical / bio-chemical source of acetaldehyde remains to be discovered.

5. Acknowledgements

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6. References

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