

Recent Findings in Acetaldehyde Emission from Leather

by

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Abstract

Acetaldehyde emissions are a significant challenge for automotive leather producing tanneries. This is especially true to meet the requirements for the Chinese market. Unlike formaldehyde, acetaldehyde is not used as a building block of tanning agents or auxiliaries and has rarely been traced in extraction assays in which the detection medium is water. However, it contributes to significant problems in emission tests for leathers in which the molecules are detected in the air. Until recently, few data points on acetaldehyde emissions were available, mostly on finished leather. In this publication, our new, facile method for the measurement of acetaldehyde emission will be introduced, evaluated, and exemplified with data across the whole process of leather making, from beam house to finished leather. With our new method we could show that the emissions generally decrease from skin to crust. Biochemical background for the high levels of acetaldehyde in skin will be given. Through the application of suitable scavengers, acetaldehyde emissions could be reduced significantly in automotive leathers.

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 to compare the contribution of products.

Experimental

In guideline 275 of the Association of the German Automotive Industry (VDA 275) aldehyde emission can be determined. In this test, a piece of leather is stored in a closed bottle. Water at the bottom of the bottle is analyzed for aldehydes after a defined time and temperature profile. In these tests only a few ppm acetaldehyde is 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. The assay conditions of the companies vary in volume of the chamber, heating conditions, size of the leather, and evaporation conditions. We developed a chamber on the basis of a rotation evaporator in which pieces of leather can be analyzed. A leather piece of eighty square centimeters remains in the flask connected to the rotation evaporator at eighty degree Celsius water bath temperature and is conditioned for thirty minutes. The volume of the rotation evaporator is in total 2,7 liters. After conditioning the air is removed from the chamber via evaporation pump and aldehydes are derivatized with dinitrophenyl hydrazine to the corresponding dinitrophenyl hydrazones in a cartridge³ positioned between the rotation evaporator and the pump, as shown in Scheme 1. The hydrazone is washed off the cartridge with acetonitrile and quantified via calibration curve on a HPLC similar to the quantification in VDA 275. The weight of the leather piece is recorded and this way the amount of acetaldehyde emission can be related to either weight or area.

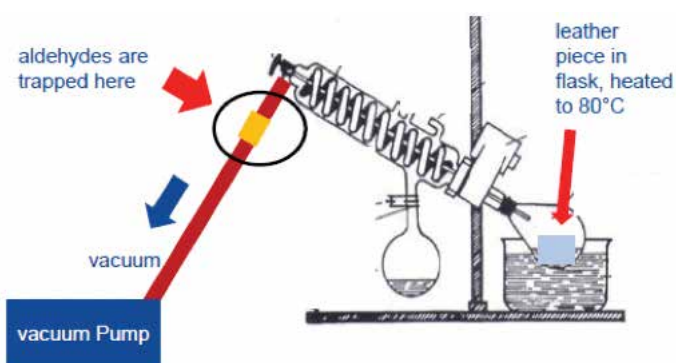
Results and Discussion

Acetaldehyde is a natural product. It is for example an intermediate with a short half-life in the yeast mediated degradation of sugar to ethanol.⁴ In the human liver the enzyme CYP2E1, belonging to the superfamily of cytochrome P-450, converts ethanol into acetaldehyde,⁵ which in the body has only a brief half-life, before it is oxidized to acetic acid.

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From collagen acetaldehyde can be released within the degradation of threonine, forming glycine and acetaldehyde⁶ catalyzed by threonine aldolase, as depicted in Figure 1. Threonine aldolase will very likely be present in the living mammal, but that this enzyme can still catalyze the release of acetaldehyde in leather is very unlikely, since it will be inactivated and separated in the beam house process. Unlike glycine or proline, threonine is one of the rarer amino acids in collagen.⁷ According to the work of Eastoe it occurs with a mass of 2,2 g in 100 g of ox hide.⁸

Initial measurements revealed that the acetaldehyde emissions are highest in the early stages of leather making like raw hide 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, meaning if the emissions would be correlated to



Scheme 1. Acetaldehyde determination in a rotation evaporator.

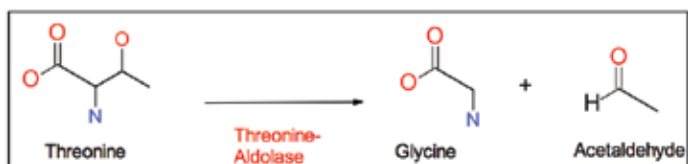


Figure 1. Degradation of threonine.

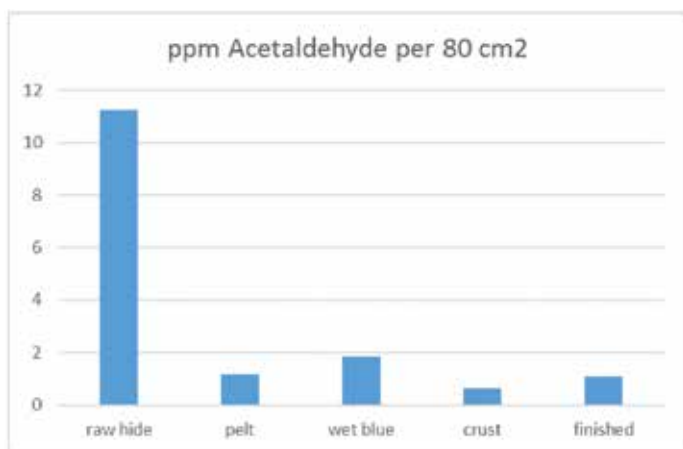


Figure 2. Acetaldehyde emission in five stages of the leather making process.

dry weight, the differences between wet blue and crust would be smaller. After finishing acetaldehyde emissions rise marginally, as can be seen in Figure 2.

These findings are in line with chamber measurements at the FILK institute in Freiberg, Germany. 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 (finish C) the values of acetaldehyde emissions stayed the same in a period of ten month, as depicted in Figure 3.

A comparison of wet blue with wet white revealed that the two intermediates do not differ significantly but that the subsequent process steps like crust and finished leather show lower acetaldehyde emission in the wet white process. The data is depicted in Figure 4.

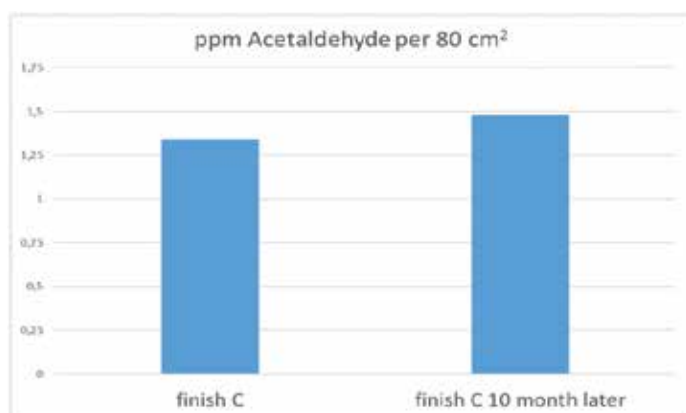


Figure 3. Acetaldehyde emission from finished leather over a time of ten month.

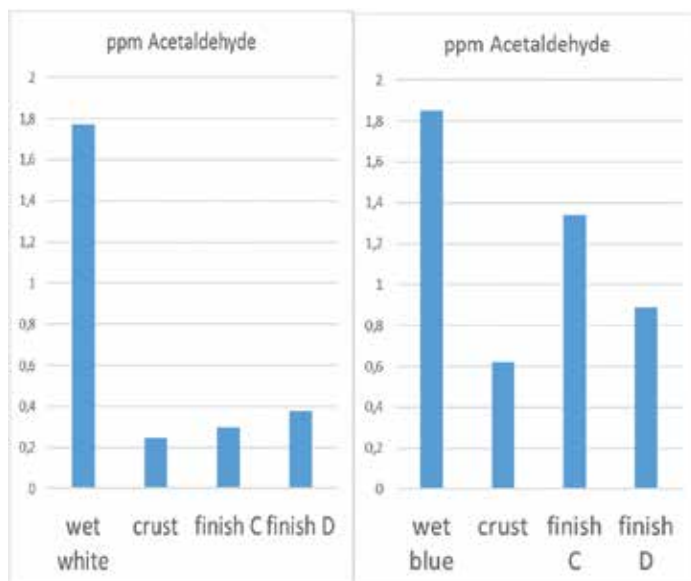


Figure 4. Acetaldehyde emission from wet blue and wet white.

An explanation for this finding can be given through a similar binding mode of glutaraldehyde and acetaldehyde. Both can be bound in a covalent manner through lysine residues in collagen in form of an imine, meaning the oxygen of the aldehyde is replaced by a nitrogen from lysine, as depicted in Figure 5. This binding of acetaldehyde in a covalent manner would explain the fact that acetaldehyde does not evaporate from leather, as would be expected taking only the boiling point into account. In the wet white process glutaraldehyde and acetaldehyde compete at the lysine binding site, as indicated in Figure 5. There are two forces in favor of glutaraldehyde competing with acetaldehyde. A kinetic one due to the excess of glutaraldehyde in the tanning process and a thermodynamic one, due to a more stable construct of glutaraldehyde, being able to bind with collagen on both end of the bi-functional molecule. In combination, these forces help to release acetaldehyde and lower the subsequent emissions from wet white based leather articles. As also visible in Figure 5

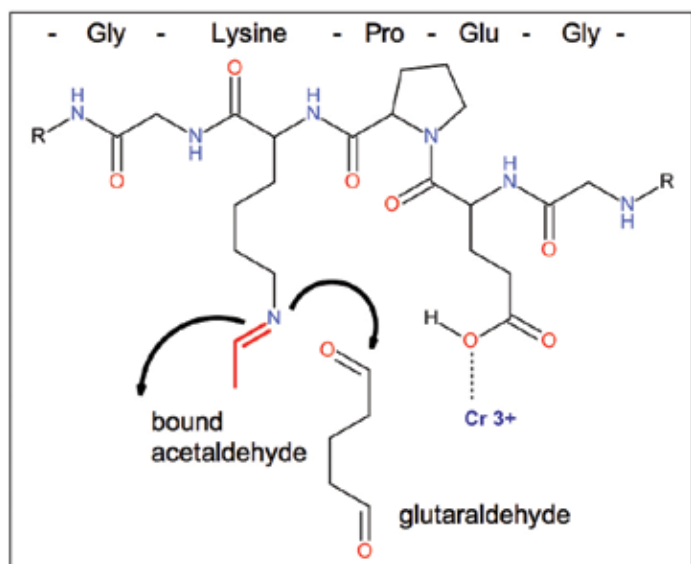


Figure 5. Glutaraldehyde competes with an acetaldehyde (in red) being bound to a lysine moiety via imine bond.

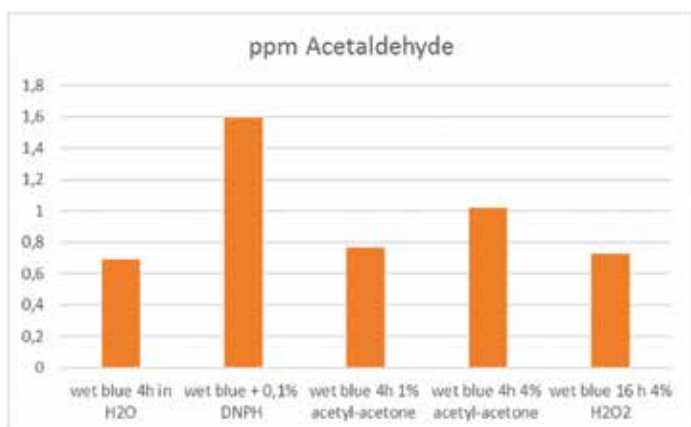


Figure 6. Scavenging of acetaldehyde with DNP and acetylacetone.

chromium interacts with glutamic acid (Glu) and therefore does not compete with acetaldehyde, explaining the higher amounts of acetaldehyde in leathers deriving from a wet blue process.

In order to measure aldehydes in extraction assay like VDA 275 or ISO 17226 the aldehydes are reacted with either dinitro-phenyl-hydrazine to yield the corresponding dinitro-phenyl-hydrazone or acetylacetone. Both reactions are used in analytical methods for the quantification of aldehydes.^{9,10} Interestingly, we were not successful in applying these reactions to scavenge acetaldehyde out of leather. As can be seen in Figure 6 application of 0,1 percent dinitro-phenyl-hydrazine (DNPH) based on the weight of wet blue or applying 1 – 4% acetylacetone did not lower acetaldehyde emissions. We gave a time frame of four hours for the reactions to take place at a pH of four. Adding the standard oxidation reagent hydrogen peroxide to a float with a wet blue did not result in lower acetaldehyde emissions. The idea behind this assay was that the hydrogen peroxide would oxidize the acetaldehyde to acetic acid.

Although the initial result with scavenging of acetaldehyde were everything else than encouraging, we continued to screen for scavengers. Finally, and surprisingly we found two versatile moieties. Product A gave unsatisfactory results if used in wet end but remarkable results if used in finishing in a flesh side application with one percent active matter on crust weight.

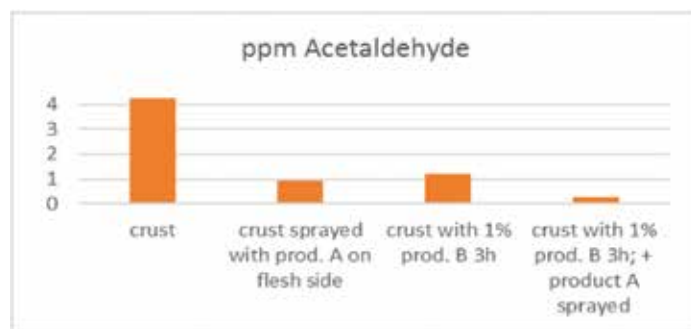


Figure 7. Scavenging of acetaldehyde in wet end and finishing.

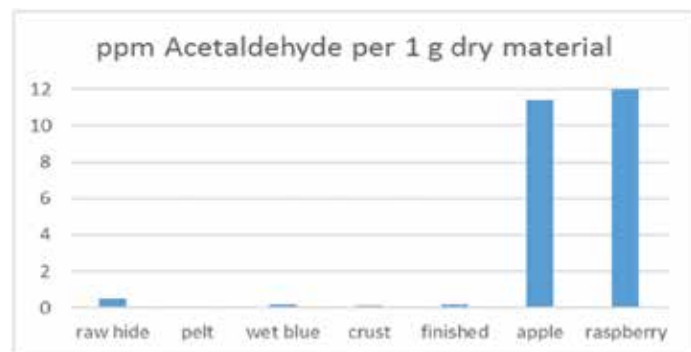


Figure 8. Acetaldehyde emissions in leather process compared to apples and raspberries.

Product B gave very promising results if applied in wet end with one percent active matter based on crust weight. Time of application of three hours gave optimized results, with more time leading to unchanged acetaldehyde values and less time resulting in higher emission values. Fortunately, the subsequent application of both products led to synergistic results having achieved a ninety percent reduction of acetaldehyde emissions (Figure 7).

It can be concluded that generally acetaldehyde emissions decrease from skin to crust and can be reduced there through scavenging in wet end process (product B) or by flesh side application of a finishing product (product A). However, the level of acetaldehyde emissions from leather are only marginally compared to a level emitted by fruits like apple or raspberries, as depicted in Figure 8. The data assembled there is on the basis of one gram dry material.

Conclusions

We established a method to monitor the acetaldehyde emissions within the process of leather making. While emissions are high in early stages, like raw hide, they are minimized on crust basis. After finishing acetaldehyde emissions rise marginally and can be reduced through adequate scavenging.

We managed to reduce acetaldehyde emissions via suitable scavenging with two products in a synergistic way and elaborated a biochemical explanation how acetaldehyde can remain in leather during basically all steps of leather manufacturing through covalent bonding.

Editor Note: For more information on the products A and B contact the author.

Acknowledgements

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