MINIMIZING EMISSIONS OF AUTOMOTIVE LEATHER

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Abstract. Today, automotive leather has to meet a multitude of requirements. One of these parameters are the Volatile Organic Compounds (VOC) which the final leather article emits. The recurring question of how to further reduce the emissions of automotive leather is answered by presenting the latest crosslinker development as one focus of this article. Nowadays, the focus of the regulations has switched more and more from quantity of emissions to the properties of single substances emitted. Often the exact source of those single substances were initially unknown and consequently a specific solution to meet the limits was not available. The search for the sources is becoming increasingly complex and difficult as many of these substances are not applied directly but are often degradation products of other compounds. Often the measured low concentrations are in the range of the natural decomposition processes. Nevertheless, it is possible to identify some of the sources by evaluating the results of different analytical methods. Thus it is now possible to develop suitable countermeasures. The presentation of the source of acetaldehyde as well as the reduction of this component in leather forms a further focus of this article.

1 Introduction

Today, automotive leather has to meet a multitude of requirements of different automotive brands. In addition to the still important traditional aesthetic properties, such as the feel and appearance of the leather, a growing number of measurable specification parameters have been added over time. These analytically measurable specification variables can be subdivided into physical ones, such as rub fastness or light fastness and chemical requirements. The chemical restrictions can be further subdivided into substances that can be extracted from the leather with a solvent such as Cr(VI) or azo dyes and substances that are emitted from the leather. This latter group includes the subject area of this article, the Volatile Organic Compounds (VOC).

2 Background of VOC's

The starting point for the problem of interior emissions from vehicle interiors was so-called "fogging". This is a condensate of low-volatility compounds that can deposit on the inside of windscreens and thus restrict the driver's view. This topic was associated with a clear, safety-relevant aspect. To reduce this phenomenon, automobile brands introduced simple tests that measure either the weight of the condensate (gravimetric) or the effect on the light transmission of the precipitate (reflectometry). These methods were the starting point for the introduction of many other tests with the aim of determining the composition of the condensate more and more precisely.

Today, most VOC analyses are performed with gas chromatography and mass spectrometry detection, which leads both to the quantification of emissions and to the identification of many individual components. Over time the focus of the emissions issue has shifted from, as mentioned earlier, purely safety considerations to the general air quality of the vehicle interior and, as the latest in the field, the regulation of individual substances for toxicological reasons.

3 The Challenge

The fact that each individual automobile OEM has developed its own test program has led to the introduction of a variety of different emission regulations and limits. Today, this method and specification "jungle" poses a major challenge for the development of automotive leather [Fig 1].

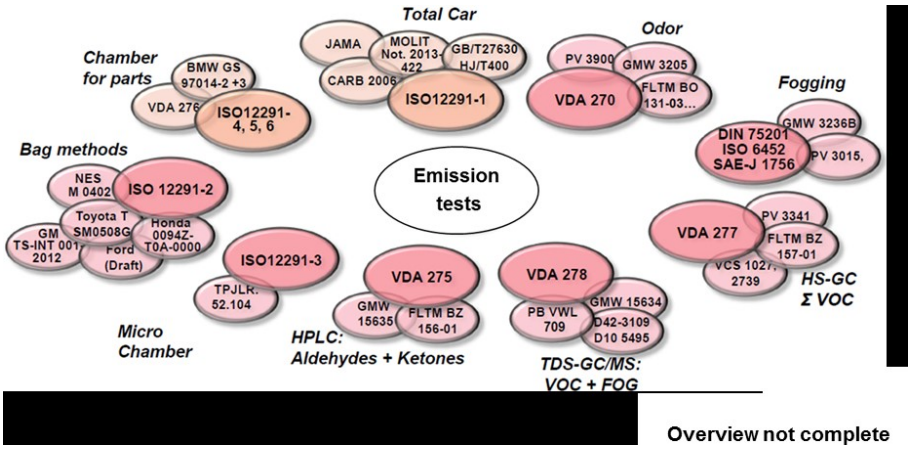

Fig. 1. Overview of emission tests.

Each of these methods has a slightly different substance focus and highlights a different group of volatile substances in the test result. For this reason, the individual methods cannot be compared. This is a big challenge, because nowadays one has to develop an automotive leather article with the very high demands on low emission values under consideration of the required test methods/limits. In order to be able to fulfil all the required parameters, it is necessary not only to have a sound knowledge of the required test methods, but also to have detailed knowledge of the products used.

4 The Trend

Due to the implementation of profound measurement of emissions over the last one and a half decades, it has been possible to reduce the emitted substances by a factor of 10 or more. As a result Total Volatile Organic Compounds (TVOC) have been reduced over time from grams to micrograms per kilogram of leather. This dramatic reduction in intensity has been made possible by the introduction of product solutions in the individual areas of both crusting and finishing products. This significant reduction is visualized in [Fig 2].

As a result, the emissions today are no longer determined solely by the products used, but are also increasingly influenced by natural, product-independent sources. These sources can be components of the hide or its degradation products or compounds which are introduced into the leather through the increasing use of sustainable processes such as fleet recycling. This means that nowadays, in addition to the still important aspects of the products used, the entire process for the production of automotive leather must also be taken into account to an increasing extent.

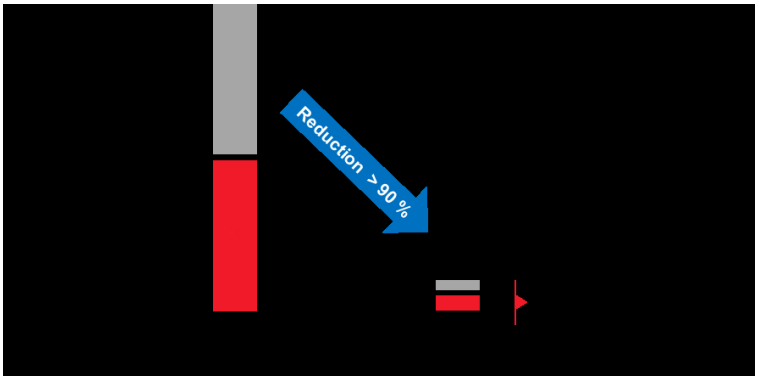

Fig. 2. Scheme of VOC contribution in different sectors.

5 Crosslinker: latest developments

Crosslinkers are an example of the range of solutions that are constantly being optimized to further reduce leather emissions. The content of solvents, which contribute to the emitted substances in the common test methods, has been further reduced in the course of time. As the latest development, the required content has been reduced to 0%, thus completely eliminating the solvent from the product. If one now prepares automotive leather with the different available crosslinkers, one measures in the usual emission test methods a clear reduction of the values. The TVOC of an automotive leather could be reduced in one example by measuring with the test method: ISO 12219-2 (10 l bag-test) from originally 66 g/sample when using a crosslinker with 50% solvent to 27 g/sample when using a crosslinker with 0% solvent content [Fig 3]. This strong reduction of 59% is more than one would normally expect. In order to understand this unusually large reduction, it is necessary to take a closer look at the individual regions of the spectrum. As expected, there is a significant decrease in emitted solvent molecules which can clearly be attributed to the solvent content of the crosslinkers used. In this example, however, this accounts for only about 72% of the measured TVOC decrease. The missing rest are mostly lower siloxanes-emissions. This is surprising as this group of substances has nothing to do with crosslinkers. The reduction of these substances can therefore only be explained by so-called "entrainment" of the siloxane molecules by solvent substances during the test. In the end, there is a synergistic effect in which other, less volatile substances are not measured in the emission test by reducing the solvents used in the crosslinkers and thus a disproportionate reduction in emissions is achieved.

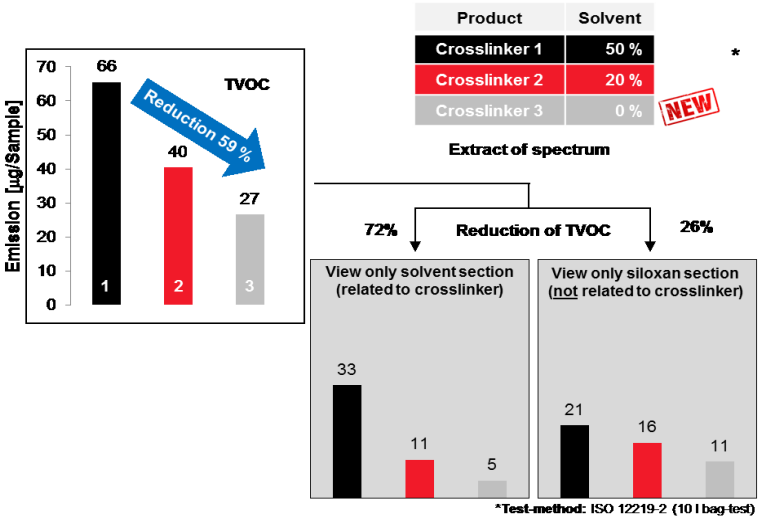

Fig. 3. TVOC values of automotive leathers using different crosslinker with different solvent content.

6 Single substance regulations: Acetaldehyde

The new China Vehicle Interior Air Quality (VIAQ) standard can be regarded as one of the latest examples of the trend towards increased regulation of individual substances emitted from leather. This standard regulates 8 substances with limits and related test method for car interiors (Fig. 4). Following the publication of the first proposal a few years ago, OEMs have already taken these regulations as a basis and adapted their individual leather specifications with stricter limits and harsher test conditions. If you now take a closer look at the controlled substances, the limit value of 7 of the 8 substances for leather can be adhered to. The only exception was and still is acetaldehyde.

List of new Chinese VIAQ limits regulated 8 Substances for car interior	Substance	Limit [mg/m³]
	Benzene	0.06
	Toluene	1.00
	Ethylbenzene	1.00
	Xylene	1.00
	Styrene	0.26
	Formaldehyde	0.10
	Acetaldehyde	0.20
	Acrolein	0.05

Fig. 4. Chinese new Vehicle Interior Air Quality (VIAQ) standard.

The problem was that the sources of this substance were initially completely unknown. Acetaldehyde is neither used directly in the leather production process nor indirectly, since it is not used in industry as a raw material for the manufacturing of chemicals for leather production. Consequently, due to the lack of knowledge where this molecule comes from, a solution to meet the limit was not available at that time.

7 The source

The interpretation of results from FILK gave the first hint about one source of acetaldehyde. This research institute found out that the highest acetaldehyde value is measured in the raw hide and the concentration decreases until the leather article is finished. One theory explaining this phenomena is the decomposition of proteins already in the raw hide[1]. Nevertheless this means that the Acetaldehyde molecule is already present in the raw hide.

However, this may not be the only source for this molecule, as the measurement of a leather after 4 months of storage showed. A closer look at all emitted aldehydes shows that all concentrations increase and that all these substances are replicated after the leather is finished [Fig 5]. The later the compound is in the homologous series, the stronger is the increase percentage wise. This is understandable, since due to the higher molecular mass of the molecules the volatility becomes lower and the relationship between formation and emission shifts to higher concentrations. The source of all these aldehydes, from hexanal to nonanal, is known and can be traced back to the degradation of natural, unsaturated fatty acids. The increase in the concentration of acetaldehyde after storage also speaks for the degradation of fatliquors as another source. The high volatility explains why the increase is lower than for other aldehydes.

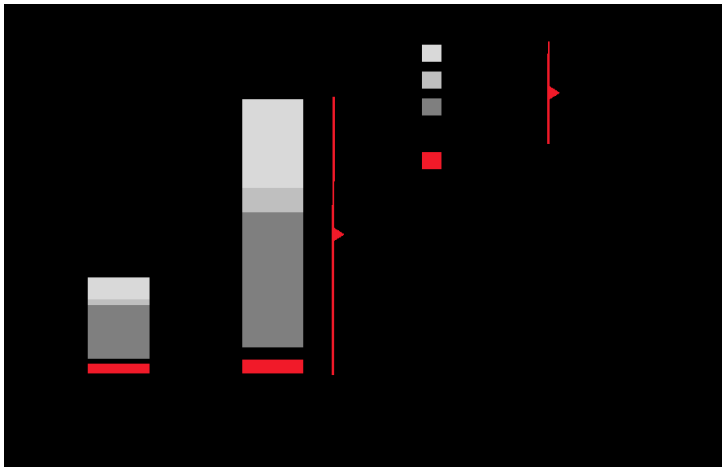

Fig. 5. Aldehyde values of a leather after storage.

To clarify the theory of whether this is really another source, 4 crust leathers were made, all from the same hide and produced in the same way. The only exception was the use of fatliquors. In one quarter no fatliquor was used and the other quarters used fatliquors with increasing natural content and therefore unsaturated fatty acids. Acetaldehyde concentrations were then measured using the VDA 277 emission method [Fig 6]. The measured concentrations increased compared to the crust leather without fatliquor and the value was more than doubled in one case. Since the samples all come from the same rawhide, the values should be similar if this were the only source. The increase in values can therefore only be explained by the degradation of fatty acids as a further source of acetaldehyde.

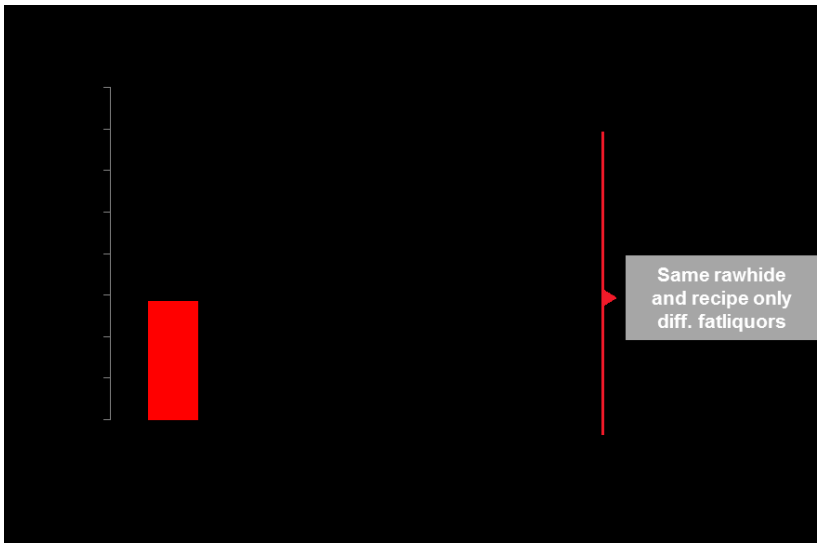

Fig. 6. Acetaldehyde values of a Crust-leather coming from one raw-hide and prepared with different fatliquors.

8 Independent confirmation

The trial series of the production of crust-leathers with different softening products was continued and, as expected, a relatively wide variation of acetaldehyde values can be found. To substantiate the theory of degradation of fatliquors as a another source, further independent confirmation by another measurement method would be desirable. For this reason, the undyed leather obtained was subjected to a heat yellowing test. In general, the results of the heat yellowing tests depend on various factors. The vegetable tanning agents, syntans, dyestuffs and fatliquors/polymers used

have an influence on the final result. In the case of the crust leather examined here, these influencing factors were limited purely to the influence of the softening products used, since all other products were the same.

In the case of fatliquors, it can be stated in general and somewhat simplified terms that a poor evaluation of heat yellowing indicates a high degradation rate or vice versa. A comparison of the values obtained for heat yellowing with the acetaldehyde concentration reveals a good correlation between the results [Fig. 7]. Crust leathers with a low heat yellowing rating, i.e. a fatliquor that is easier to degrade, also have high acetaldehyde concentrations. In contrast to this, a good heat yellowing rating is achieved when using more stable fatliquors/polymers softeners and a correspondingly lower acetaldehyde value is measured. Thus the theory is confirmed by a further, independent measurement. However, it must be emphasized again that the correlation of heat yellowing with acetaldehyde values is only possible within the framework of the selected test program, excluding the other influencing factors. Otherwise, this correlation is generally not possible due to the many existing variables.

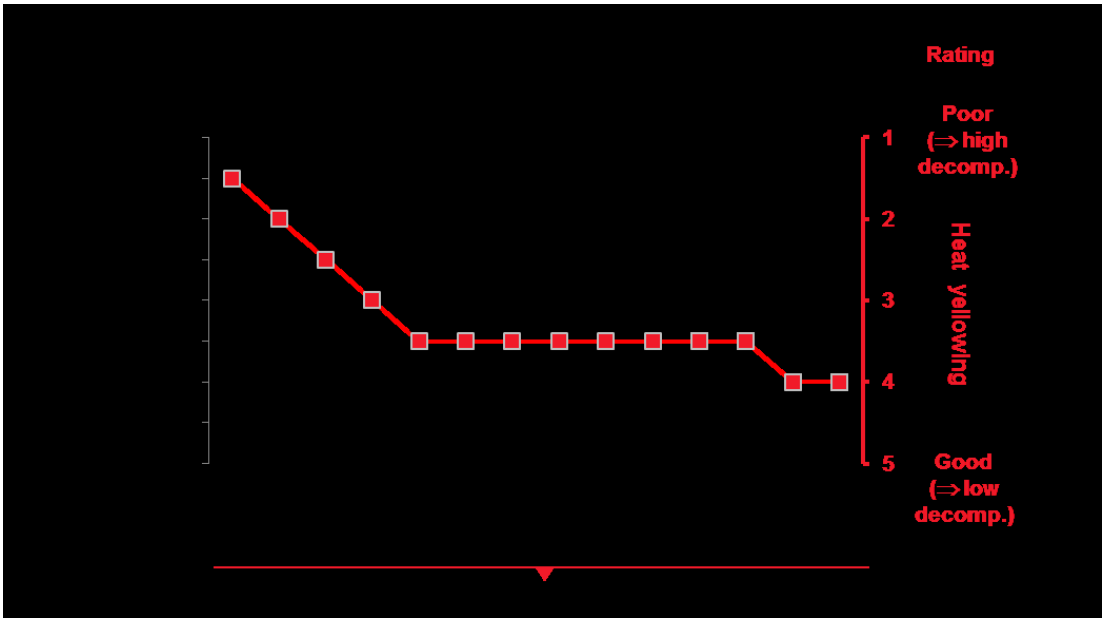

Fig. 7. Correlation of emission test and heat yellowing rating.

9 Available technical solutions

After identification of the two sources, suitable products could be developed to lower the measured concentrations of acetaldehyde and thus meet the required limits for this substance [Fig. 8]. Among others, special syntans are offered which can wash out aldehydes including acetaldehyde coming from the rawhide of the wet processes. In order to minimize the other source, the degradation of fatty acids, a special polymer softener can be used in the retannage to prevent the formation. Also special flesh side binders are offered to lower the substance coming from both sources directly. Such products can also be understood as a modular system.

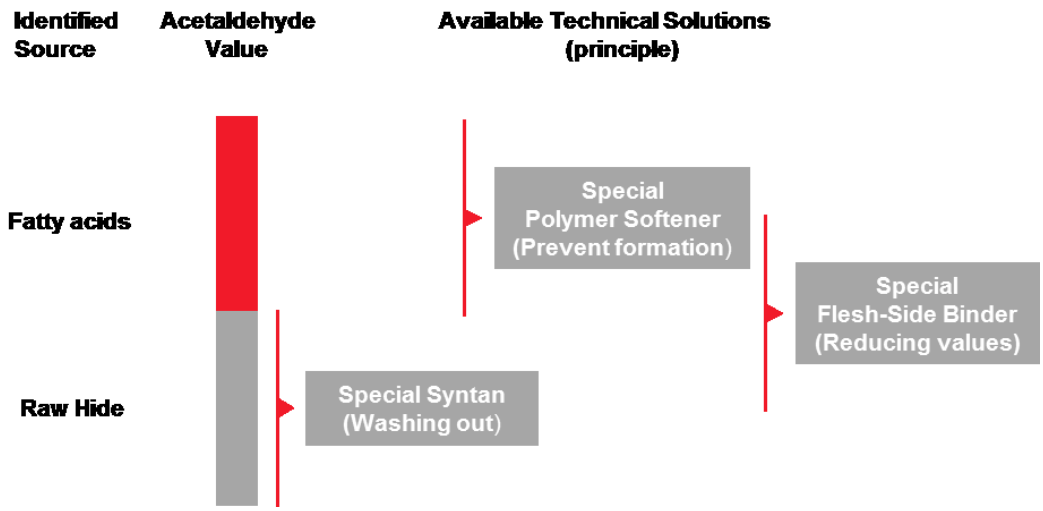

Fig. 8. Sources and possible solutions to reduce Acetaldehyde at a glance.

The following experimental concept was chosen to examine the extent to which the newly developed auxiliaries can reduce emittable substances [Fig. 9].

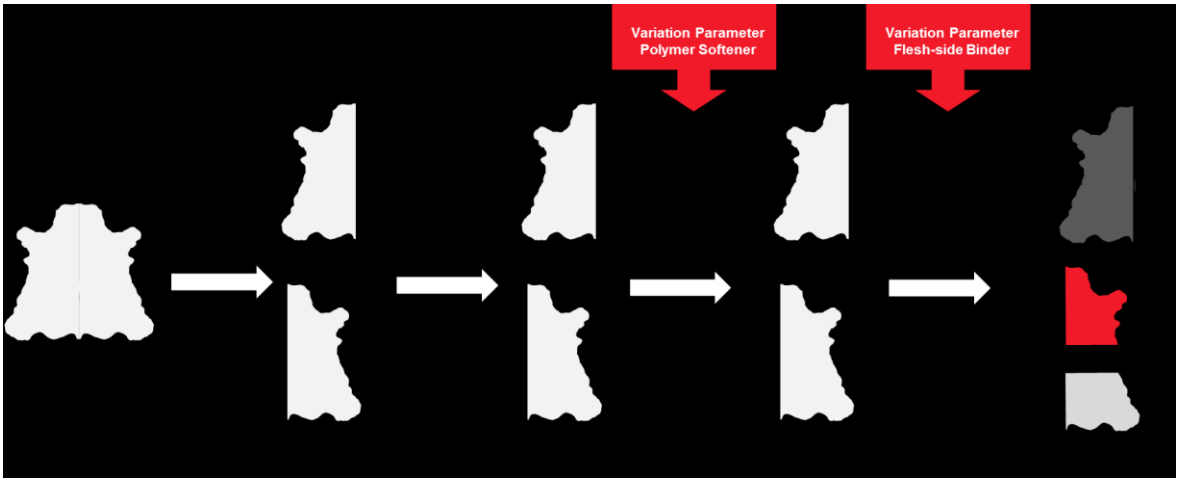

Fig. 9. Trial concept: to proof modular concept two possible parameter were changed.

The same wet blue was divided and retanned with the same reciepe and products. The only exception was the softening products used. In one half the fatliquor was partially replaced with the special Polymer Softener. Subsequently, the two crust-leathers obtained were finished, whereby in one case the Flesh-side binder used was replaced by the specially developed one. Subsequently, the emissions of all samples were measured using the ISO 12219-2 method (10 l bag-test). The result shows that with the products not only the values for acetaldehyde and aldehydes in general are reduced, but also the total emission can be minimized [Fig 10].

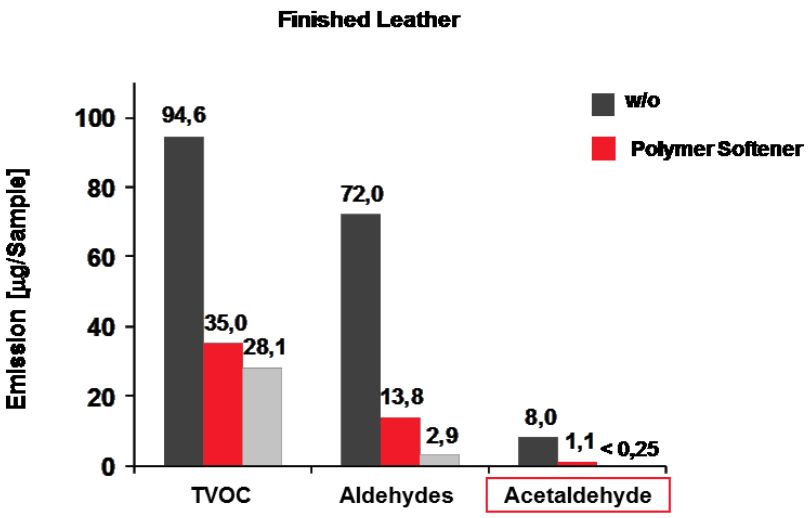

Fig. 10. Impact of auxiliaries integration in recipes.

10 How to minimize Emissions

Let us summarize the answers of how to minimize emissions from automotive leather. As is so often the case with leather issues, the entire manufacturing process must be taken into account to answer this question. The minimization of the VOC's starts already in the Beamhouse, continues with points that have to be considered in the retannage and finally the finishing system has to be considered [Fig. 11].

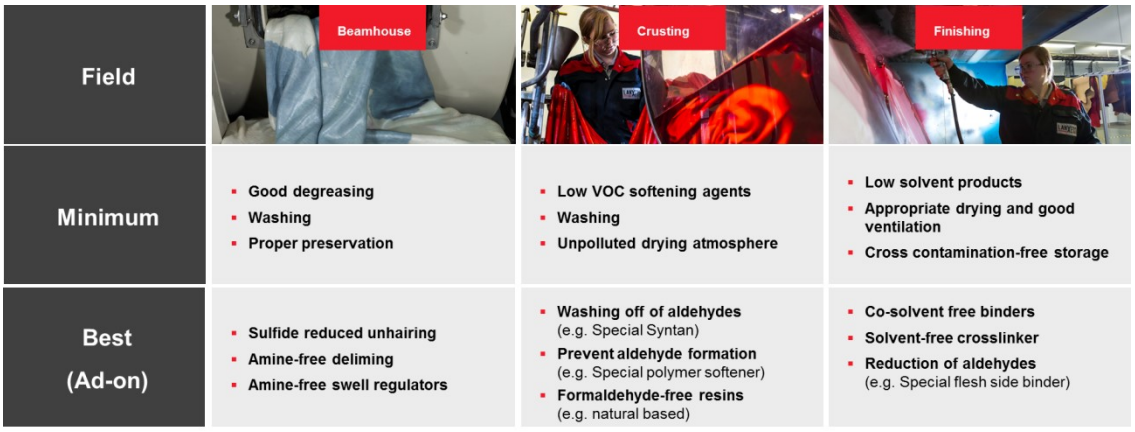

Fig. 11. Overview how to minimize emissions in automotive leather.

11 Conclusion

Nowadays, in the context of emissions, in order to meet the high requirements and all the required parameters, it is necessary to have a sound knowledge of the required tests and the associated focus of these methods. Furthermore, detailed know-how of the products used for the leather article is required. Through the development of ever better, VOC-optimized solutions, such as the solvent-free crosslinker presented in the article, the concentration of emitted substances from leather can be further reduced. In this case, the reduction is bigger than expected due to the

reduction of the solvent content alone. This trend towards reduction on the product side will continue. However, total emissions today are no longer determined solely by the products used but are also increasingly influenced by natural sources. Many of today's individual substance regulations are in the range of natural degradation processes. This complicates the search for sources, as many limited compounds are no longer used directly or for the production of leather chemicals. Many measurements and their conscientious evaluation are necessary for the detection in order to develop suitable solutions. This may take some time and, as in the case of acetaldehyde, may result in satisfactory solutions being available only after regulation of such substances. Nevertheless, the minimization of emissions from leather is a real success story in which the values found have been massively reduced in recent years.

References

1. Ammen, J. Wegner, B. Dannheim, B.: Recent Findings in Acetaldehyde Emission from Leather, JALCA, 112, 2017