



VOC-free leathers: A moving target

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Emissions of Volatile Organic Compounds from leather originated as a discussion in the automotive industry, triggered by so-called "Fogging", a physical effect. Nowadays the focus is increasingly on smell and toxicological aspects of VOC emissions. This calls for new tests and bringing substances into the spotlight that have not been considered before. The intent of this paper is to give a short overview of current testing of emissions from leather, and especially new challenges associated with acetaldehyde and propylene glycol ether - fogging problems once considered to be solved that have surfaced again.

In 1999 the use of volatile organic compounds (VOC – defined in *Panel 1*) in industrial processes was regulated in Europe by the "solvent" directive 1999/13/EC. When applied to leather, this limits the maximum amount of solvents used for the entire production process to 75 g/m². The focus of this directive is to protect the environment and population from excessive emissions into the atmosphere.

Today, for standard leather articles, this limit is no longer a

Panel 1: VOC-definition for Europe

According to 1999/13/EC, VOC shall mean any organic compound having at 293.15 °K a vapour pressure of 0.01 kPa (0.1 mbar resp. 0.075 mm Hg) or more, or having a corresponding volatility under the particular conditions of use.



Panel 2: Overview of common test methods, emission focus and source.

Number	Equivalents	Principle	Condition	Focus	Main Source
ISO 17071	Fogging	Evaporation -> condensation; gravimetric / reflectometric	100°C	Low volatile substances	Crust (Fatliquor)
VDA 278	VOC / Fog Daimler-method	Dynamic headspace, GC-MS detection	90°C / 120°C	Medium and low volatile substances	Crust (Fatliquor, Auxiliaries)
VDA 277	TVOC Volkswagen-Method	Static headspace; GC-MS detection	120°C	Medium volatile substances	Crust, Finish (solvents), decomposition products
VDA 276	BMW Summer-Test; Toyota-Method	Test chamber; GC-MS detection	65°C	All substances	Crust, Finish (solvents), decomposition products
DIN 16000	Blue Angel	Test Chamber, GC-MS detection	23°C	Medium volatile substances	Finish (Top coat)

problem, and solvent emissions from production are lower by one order of magnitude or more. It is nevertheless legally mandatory in Europe and requested globally on a voluntary basis (the LWG environmental audit protocol to collect and report the information about solvents used during manufacture). As most solvents have to be labelled one way or the other, chapter three of a GHS material safety data sheet will give a good first approximation if the supplier does not provide a declaration or technical product information that contains the necessary information.

Emission Tests

At the same time as the “solvent” directive 1999/13/EC, the automotive industry started to look at leather as a source of emissions that added to the so-called fogging effect, a condensate that forms on the inside surface of the windscreen especially of newly fabricated cars when they are subjected to temperature changes.

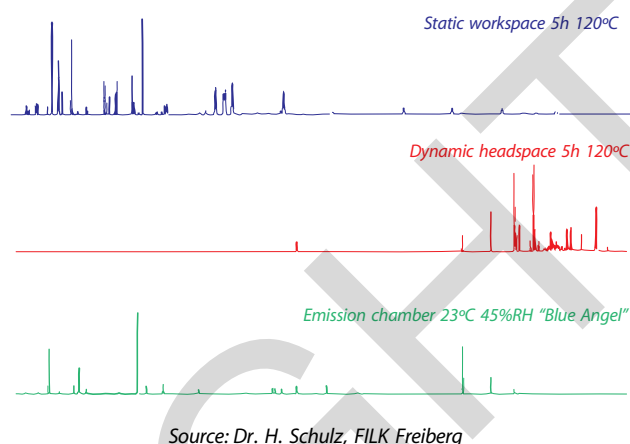
The general test DIN 75201 was specified for leather as DIN EN 14288 (today ISO 17071). For the first time attention was given to the fact that various substances may have a different effect by rating the fogging according to simple mass, or by how much their condensate reflects the light.

The correlation of both of these values is poor and the method itself limited in potential. There is no information on the identity of substances in the condensate – and with that potential toxicological effects – but an engineer’s focus to the obvious risk of driving a car at reduced visibility.

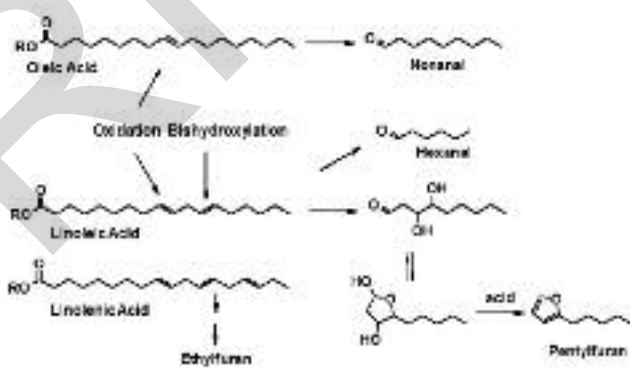
VDA 277, known as “Volkswagen-Method” or “TVOC-determination”, and VDA 278 “Daimler-Chrysler-Method” or “VOC/Fog”, are two miniaturised headspace emission tests. These both use a Gas Chromatograph with Mass Spectrometer detection to quantify the emissions and identify the single components. The emission is forced by elevated temperatures of 90° and/or 120°C, thus simulating fogging conditions, but reducing the relevance of the values for any evaluation of potential toxicological impact of single substances.

That issue was finally put into the focus with development of test chamber methods such as VDA 276, BMW GS 97014-3 or DIN EN ISO 16000 9 & 10. In these methods samples up to one square meter are exposed to classical atmospheric conditions and resulting concentrations of VOC determined via Gas Chromatography. Unfortunately the testing is much

Panel 3: Gas Chromatograms: emission comparison of an automotive leather using different test methods



Panel 4: Degradation mechanism of unsaturated fatty acids from natural fat or fatliquors to form long-chain aliphatic aldehydes



more expensive than any other method and it can take up to five weeks to receive a result. This makes it very difficult to apply in development processes.

Due to these consecutive developmental steps the detection range of volatile substances emitted per kilogram of leather has gone down from the range of grams to micrograms. This has made the term VOC-free leathers a moving target. On top of the issue of quantity, there is a problem with qualitative statements, as every single method emphasises a different group of volatile substances and the measurements cannot be compared. This is illustrated in the emission comparison of an automotive leather using different methods of testing, and given as Panel 3.

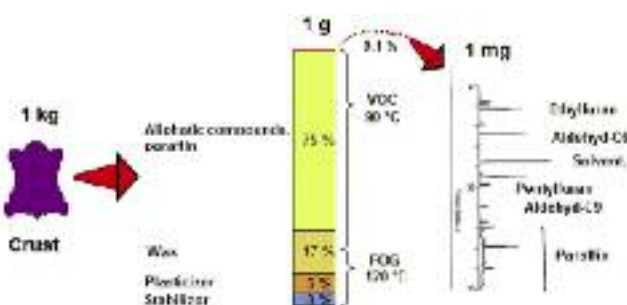
Finally, the possibility of identifying single substances has shifted the focus away from pure quantity to the properties of single substances.

A shift of focus: Toxic Trace Impurities

Formaldehyde – with well-known toxicological properties and wide dispersive presence from natural sources and use as a raw material in chemistry – was one of the first substances to attract attention. With VDA 275 for leathers and ISO 27587



Panel 5: Relation of emission quantity from a typical furniture leather analysed by VDA 278



Panel 6: Relation of emission quantity from a typical furniture leather analysed by VDA 278

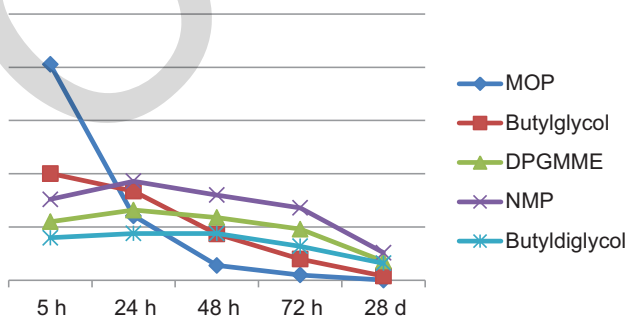
Leather	A	B
Test Method	VDA 277	GS 97014
Substance	[$\mu\text{g C / g}$]	[$\mu\text{g / m}^3$]
Formaldehyde		7
Acetaldehyde		11
Propanal		13
Hexanal	5	67
Nonanal	1	119
Other aldehydes	4	22
Furanes	7	
Total Emissions	55	760

Note: units of emissions are different for both tests

Panel 7: Some commonly used glycol compounds (in comparison to toluene, water and NMP)

	Boiling point [°C]	Rel. evapor. rate [BuAc = 1]	Heat of evaporation [J/g]	Vapor pressure [mm Hg @ 20°C]
Acetone	56	5,600	546	184,52
Toluene	111	2,000	347	21,75
Iso-propanol	82,4	1,500	667	31,20
1-Methoxy-propanol-2 (PM)	120,1	0,700	435	9,98
Water	100	0,300	2261	17,48
1-Methoxy-2-propyl-acetate (MPA)	146	0,210	296	2,78
Diacetone alcohol	166	0,150	377	1,23
Ethyl-3-ethoxy-propionate (EEP)	170,1	0,120	291	1,13
Butyl-glycol (Butyl Cellosolve)	171,2	0,079	348	0,76
Ethylene glycol	197	0,045	798	0,06
Propylene-glycol-diacetate (PGDA)	191	0,040	259	0,23
N-Methyl-2-pyrrolidone (NMP)	204,3	0,030	550	0,24
1-Methoxy-di-propylene-glycol (DPM)	190	0,020	267	0,28
Di-ethylen-glykol-monomethyl-ether	194	0,019	369	0,19
Butyl-diglycol	230	0,004	327	0,03

Panel 8: Fading characteristics under test chamber conditions for selected solvents



for tanning agents, it even has its own specific test methods for emissions.

A wide variety of threshold values proposed by NGOs or required by brands are far more restrictive than the “No Effect Levels” that have been derived by authorities and industry based on toxicological studies. Sometimes the additional safety margin is in the range of three orders of magnitude, taking the threshold below average ambient air concentrations.

Nevertheless, looking at test results and failure rates, it can be said that for leather the formaldehyde situation is well under control. Even with these thresholds the leather industry can be viewed as being two steps ahead of other sectors such as the textile or building industries.

However, a more recent development has “discovered” the presence of other aliphatic aldehydes, especially acetaldehyde. Acetaldehyde is not a constituent of any leather auxiliary that we are currently aware of, but only found after analysing leather samples under certain test conditions. Moreover, and it is not quite clear yet, how much of the problem is the result of the analytical testing method(s) involved.

The longer chain aliphatic aldehydes, such as hexanal or nonanal have long been recognised as an integral part of typical leather smell. They are created when unsaturated compounds such as fatty acids are oxidised during storage of the leather, as indicated in *Panel 4*, where together with oxidised phenols they result in a very pleasant aroma that is probably strongest in an old-fashioned saddlery leather.

However, compared to the total emission from a non-optimised leather detected in one of the tests under forced conditions, the absolute amount of such aldehydes and furanes is negligible, as indicated in *Panel 5*.

Nevertheless, with state-of-the-art automotive leathers having much reduced emission values, and test chamber and static headspace methods emphasising substances with higher volatility, the percentage of aldehydes in the total emission could increase to a very visible level. Examples are provided in *Panel 6* which shows the emission profile of two state of the art automotive leathers subjected to analysis using two different test methods.

Both formaldehyde and acetaldehyde levels found in leather B are in the typical range of ambient air concentration (*source: WHO Environmental Health Criteria 167: Acetaldehyde*), so in principle the test results should comfort any downstream user who has to work with such a leather. However, there are three facts coming together that do complicate the acetaldehyde situation:

- Acetaldehyde is more volatile and less reactive than formaldehyde. Virtually all acetaldehyde created through testing will emit, while part of the formaldehyde fixes to the collagen matrix.
- Being widely dispersed in the environment (as intermediate in biological ethanol metabolism), acetaldehyde has been extensively studied to identify hazards, but not as intensively as formaldehyde to quantify the risks. And so safety margins applied can easily be over-cautious and cause a so called



“ghost hunt”. Acetaldehyde in industry is not a raw material or component for any chemical for leather production as far as we are aware. However, aliphatic ethers are subject to a similar oxidative decomposition mechanism as unsaturated compounds, and breakdown of polyethylene glycol chains will result in acetaldehyde.

- Such polyethylene glycol chains are the backbone of non-ionic surfactant chemistry and present through the complete leather production chain - from degreasing in beamhouse to touch auxiliaries in finishing. They are irreplaceable and often not even identifiable as many types need no labelling and cannot be found on any product documentation.

Avoiding a failure in acetaldehyde testing is therefore extremely complex. A common starting point is an intensive washing towards the end of retannage. Using high-quality products from reliable suppliers can have a direct and an indirect benefit. Stabilisers used to increase the fastness values of, for example, a fatliquor, will also reduce the decomposition of the polyethylene glycol chain. Auxiliaries that do reduce the emission of formaldehyde may work depending on their mode of action.

Return of fogging issues: propylene glycol ethers

The glycols are not only of interest as a source for aldehydes. Low molecular weight ethylene and propylene glycols, their ethers and esters, are featured in virtually every emission analysis. The low toxic liquids have become substance of choice to replace the so-called high-boiling, polar aprotic solvents like NMP and DMF that have been state of the art in synthesis and application of water based finishing binders.

From methoxy propanol acetate to butyl diglycol polarity, boiling point and evaporation enthalpy can be selected in steps to fit the needs of the finishing preparation. Some organic solvents that might be found in aqueous finishes are set down on *Panel 7*.

And fading characteristics or loss of various solvents used in finishing from

leathers as they age also need taking into account, as illustrated in *Panel 8*.

Summary

In general, the emission characteristics of a leather are not the highest priority for selection of the solvent during binder manufacture. The decision is complicated by the question according to which test the leather will be evaluated.

For certain tests even an increase in solvent amount can be beneficial if a substance with unfavourable emission

characteristics is replaced. However, this will not work with the classical fogging test, as this achieves the most complete integration of the volatile organic compounds contained in the leather.

This is a complex and changing situation.

At present, the most effective approach for the leather manufacturer is to trust the experience of the supplier regarding which products to combine in their range to get best results for a given end customer and test combination. ☉

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