EMISSION FROM AUTOMOTIVE LEATHER - STATE OF THE ART AND A CRITICAL FORESIGHT

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ABSTRACT

Modern people spend a lot of time in cars. Therefore several tests have been developed and established to analyze the emission behavior of car trim materials and to set specifications to protect the passengers. Boehme investigated the correlation between leather processing and the test results of the different emission tests. The impact of the used chemicals as well as the influence of the most important operation steps were studied. Based on this know-how, the today established emission tests are introduced. Precautions for the production of automotive leather, which meets the specifications of the car industry, are discussed. Special investigations on the reproducibility and interpretation of the dynamic headspace test are shown. The conclusion is, that this method is a fast and economic tool for screening the emission behavior of leather. It is not dedicated for full-quantitative statements.

INTRODUCTION

Modern people spend most of their time in interiors: their residences, offices, recreational places from restaurants to fitness centers and also public and private means of transportation. Therefore over the past years the air quality of interiors has been intensively investigated with the aim to protect the human health and to set standards in clean living conditions.

Within this context, the interior of cars is a very special issue. The general trend in car design and development over the last decades has changed from a simple transport vehicle towards a "living area on wheels". With that, the average quality standard of car interiors, especially those of middle and lower class models, has tremendously increased. It is nearly unimaginable that a private car does not have any carpeting or a well designed dashboard and door trim, although these are not absolutely necessary for the original purpose as a transport medium. Also changes in the car body design towards sportier shapes have caused a tremendous impact on the interior air quality. The car windows, especially the front and rear screens, have become flatter and at the same time larger - flatter to improve the aerodynamics of cars, larger to improve the driver's view, and so to enhance safety. The negative effect was a remarkable increase of the temperature inside the cars. Due to the direct exposure of the dashboards to sunlight through the flat windscreen, the surface temperature of these trim materials rises up to 120°C. This causes not only problems in heat and light resistance with regard to shrinkage, ageing and yellowing, but also to emissions of medium and low volatile substances. Therefore the automotive industry started very early to develop and establish several test methods to evaluate the exposure to the interior air of cars and to set specifications for trim materials.[1,2,3]

Leather is a trim material which is more and more used in cars. Wherever used, it has an exclusive aspect, a high practical value and in the end an excellent image as first class material. Investigating the correlation between the processing and the emission behavior of leather, we can generally differentiate between two manufacturing processes: wet-processing and finishing. In finishing, emission is normally a problem of solvents, solutizers, plasticizers and monomer residues. In wet-processing the situation seems to be much more complex and precautions with regard to a conscious chemical selection or a special process control are more difficult. The distribution of chemicals is fairly different in both processes. Finishing should result in a uniform film on the leather surface with an overall identical chemical composition. Wet-processing, which affects the leather fibers and not only the leather surface is much more "unequal" with regard to the leather area, e.g. by filling the loose parts of a hide or by special softening the tight areas. It is almost like a reflection of the naturally uneven grown skin.

The following report introduces the established test methods for leather, the "state of the art" and precautions concerning wet-processing from the raw skin to crust leather. We concentrate on the dynamic headspace test, one of the latest established methods, and present our latest test results with a critical discussion.

METHODS AND STATE OF THE ART

Due to its complexity, the emission behavior of automotive

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leather cannot be analyzed with only one method. At the moment basically six different test systems are established.

These are:

- the odor test (better odor judgement)
- tests for formaldehyde
- the gravimetric and the reflectometric fogging test
- the emission chamber test
- the static headspace test
- the dynamic headspace test

Odor Test (Odor Judgment)

Because of the personal sensibility and subjectivity of the idividual persons involved, the odor test could be the most difficult test of all. In view of the customer satisfaction, it will be most important, because the customer will do this "test" completely unconsciously every day when using his car.

To check the odor, a leather sample is placed in a glass bottle and tempered at e.g. 80°C for two hours. Then the odor is characterized by at least three persons. The odor rating is done according to the classifications shown in Table I.

TABLE I
Odor Rating

rating 1	not perceivable
rating 2	perceivable, but not disturbing
rating 3	clearly perceivable, not yet disturbing
rating 4	disturbing
rating 5	strongly disturbing
rating 6	intolerable

Normally the specifications of car manufacturers are maximally at rating 3, that means at a clearly perceivable, but not yet disturbing odor. Only the companies Ford and Jaguar are more severe in their specification with a maximum rating 2. Generally these specifications can be met. Nevertheless it should be pointed out that at least the odor-sense differs considerably e.g. from Western Europe and North America to Asia. In cooperation with a well-known German perfume manufacturer several years ago, we found out that "Western people" favor a leather smell which is caused by the use of vegetable tannins and fish oil based fatliquors. This is quite different from the Asian taste. Therefore a very careful selection of chemicals is the first step to minimize bad leather odor.

Other sources for an unpleasant smell like residual chemicals from the liming process or catabolic products of microorganisms can be avoided by proper processing, especially by sufficient washing during wet processing, and an adequate preservation of the leather. An efficient drying and airing of the leathers will do the rest.

Formaldehyde Tests

Formaldehyde is classified as a suspected carcinogen. Due to the fact that formaldehyde-based auxiliaries are increasingly applied in the processing of special leather types, the car industry has established methods to check a possible contamination of the car interior. The emission of formaldehyde is determined with a static test (bottle method) or with a dynamic test ("Japan method"). Furthermore a test exists to determine the formaldehyde content (DIN 53315) by aqueous extraction, but this is not an emission test.

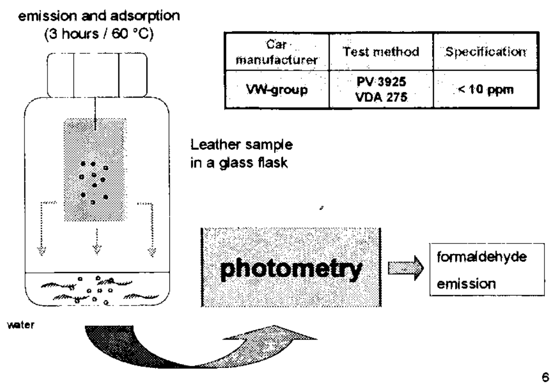

Figure 1. - Formaldehyde emission (bottle method)[6]

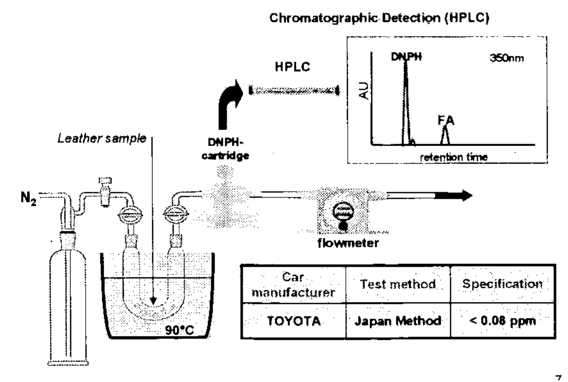

Figure 2. - Formaldehyde emission (Japan method)[7]

The test methods and the appropriate requirements of the automotive industry are shown in Figures 1 and 2. In the so called bottle test, a leather sample is suspended over water in a sealed bottle for 3 hours at 60°C. The formaldehyde concentration in the three phases - air, water and leather - reaches an equilibrium, and the formaldehyde in the aqueous phase is then derivatized and analyzed by conventional photometric techniques. The analysis conditions are fairly mild. Therefore it can be assumed that only the free formaldehyde present in the leather is detected. The spec for the Volkswagen group is a maximum of 10 ppm, which normally can be met.

Compared with the bottle method, the Japan method is a dynamic test. For this method, small leather pieces are placed in a U-tube immersed in a 90°C hot water bath. Nitrogen is led into the tube and carries the formaldehyde to a derivatization cartridge. Then the formaldehyde content is detected with HPLC technique. The specification of TOYOTA, who invented the method, is a maximum of 0.08 ppm formaldehyde.

Unlike the fogging emission test, there is no influence on the formaldehyde emission from the raw skin apart from an appropriate preservation. A very careful selection of the chemicals used in wet processing is of essential importance. Especially those chemicals which release formaldehyde or which are chemically based on formaldehyde condensation products like some pre-tanning agents, most syntans, fixing agents and resins, need to be selected and used with care. Also dye penetration and levelling agents and preservatives can cause a whole lot of formaldehyde emission because of their chemical nature. The possible formaldehyde sources and their impact are shown in Figure 3.

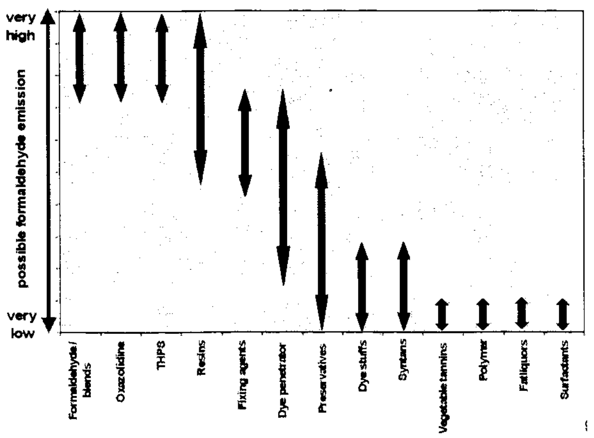

Figure 3. - Auxiliaries that cause formaldehyde emissions

Several authors[4,5] report, that it is also possible to eliminate formaldehyde by an after-treatment with oxidizing, respectively reductive chemicals, or with scavengers. We advise not to use any oxidizing after-treatment of chrome leather generally, because of the risk of a chromium(VI) formation. In our trials we found that an after-treatment with reductive agents often results in a significant shift of the color. But we can confirm, that in many examinations we found a noticeably small formaldehyde value, when higher amounts of vegetable tannins have been used or on black dyed leathers. Both, vegetable tannins and most black dyestuffs, seem to have good scavenging properties.

Fogging Tests

The fogging test was mainly established for safety aspects concerning the driver's sight through the windscreen. It is the simulation of an evaporation and a subsequent precipitation of chemicals from trim materials. Either the mass of fogging emittents is determined (gravimetric test) or the degree of opacification of a glass plate (reflectometric test). The test method is shown in Figure 4.

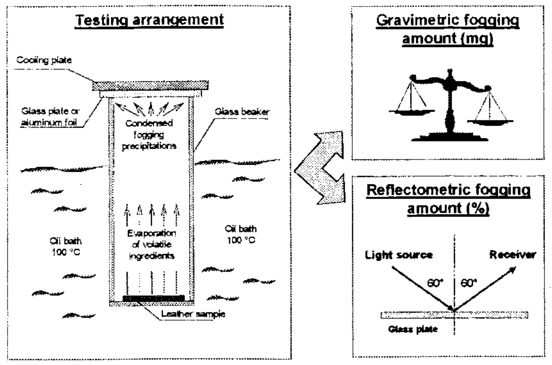

Figure 4. - Fogging test method

The specifications of the car industry for the gravimetric fogging value are between less than 3 mg and less than 7 mg, those of the reflectometric test depend considerably on the specific test parameter and are between over 60 percent and over 90 percent reflection. An overview about the current specifications is shown in Table II and Table III.

TABLE II
Specification Gravimetric Fogging

Company	Method	Specification
DaimlerChrysler	DIN 75201-B	< 3 mg
VW group	DIN 75201-B	< 5 mg
Porsche	DIN 75201-B	< 5 mg
BMW	DIN 75201-B	< 7 mg

TABLE III
Specification Reflectometric Fogging

Company	Method	Specification
Ford	SAE J1756	> 60 %
GM	SAE J1756	> 60 %
Volvo	STD 1027, 2711	> 90 %
Saab	Not known	> 80 %
Opel	GME 60 326 - B	> 90 %

The typical fogging emittents are well known[6,7] and therefore chemicals with fogging compounds can be avoided within leather processing. It is also necessary to optimize the operation steps during the production to avoid the incorporation of fogging substances. It is of main importance to select a suitable raw material as the basis for the manufacture of fogging-optimized automotive leather. E.g. natural fat, inorganic salts from the beamhouse or improper preservatives used in raw stage or wet blue and wet white stage can cause tremendous problems. As in the case of formaldehyde emission, also in case of fogging a conscious selection of optimized chemicals is a decisive factor to produce

leather which meets the standards. The fogging behavior of automotive leather is most markedly affected in wet processing by the quality of the fatliquors. An overview about the impact of wet processing chemicals is given in Figure 5. Effective scouring and rinsing during or at the end of the wet-end process are just as important as intensive final drying.

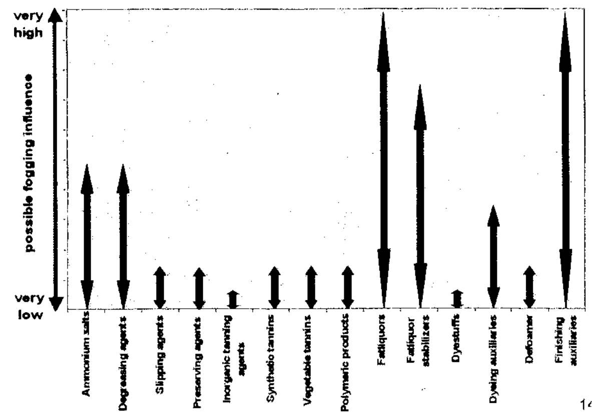

Figure 5. - Fogging chemicals

Emission Chamber Test

The emission chamber test has been primarily developed to test whole sub-assemblies up to even complete cars. Figure 6 shows a smaller emission chamber for testing smaller sub-assemblies. Generally in the emission chamber every real and unreal situation concerning temperature, time, humidity, air renewal, air speed and room charging can be simulated. The results, which are obtained online or by separate sampling, are very remarkable. By a GC-MS analysis (gas chromatography with mass spectrometry) each individual substance, which evaporates from the sub-assembly can be detected and automatically classified in groups of harmless, limited, and harmful chemicals.

At present no specifications from car manufacturers concerning the emission chamber test are known, but it is clear that no harmful chemicals should be found in the emission spectrum. Although the results of the emission chamber test are very interesting and valuable, the method has some crucial problems:

- it is not designed for routine tests and it is not possible to run it self-controlled,
- testing needs too much time (duration up to 28 days),
- it is so expensive that only car companies or important and well financed test institutes can make this investment.

Because of these problems the car manufacturers and institutes had to look for easier, cheaper and faster test proceedings. As a result the static and dynamic headspace test has been established.

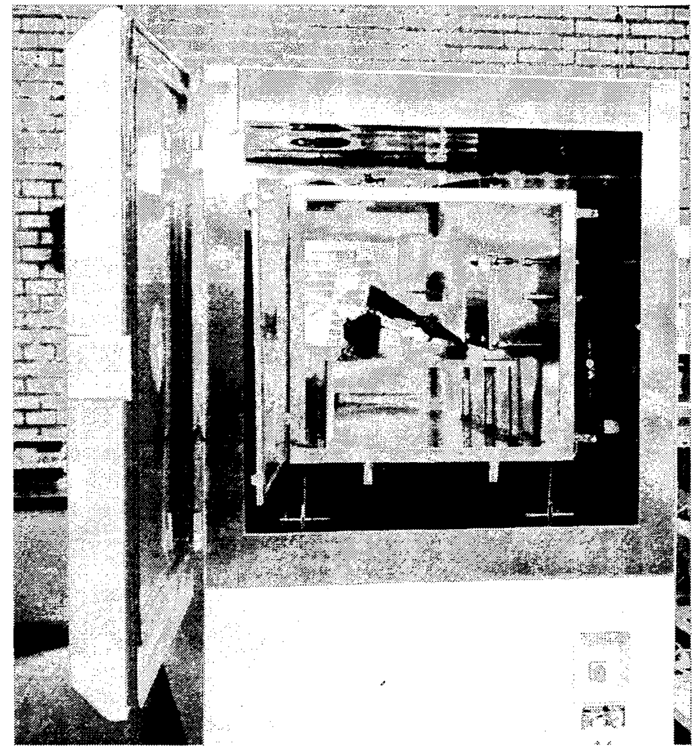

Figure 6. - Emission Chanber

Static Headspace Test

The static headspace test determines the sum of volatile and moderately volatile emittents, but without any identification of individual substances. It covers emitting substances like alcohols, aldehydes and solvents. Figure 7 shows the test method and specifications of some car companies.

Generally it is no problem to meet the specifications for leather of the static headspace test, if solvent-free or solvent-minimized auxiliaries and processes are used. Due to the volatility of the emittents, an intensive final drying is most crucial to minimize the emission.

Dynamic Headspace Test

The dynamic headspace test seems to be the attempt to scale down the emission chamber test and to make it self-con-

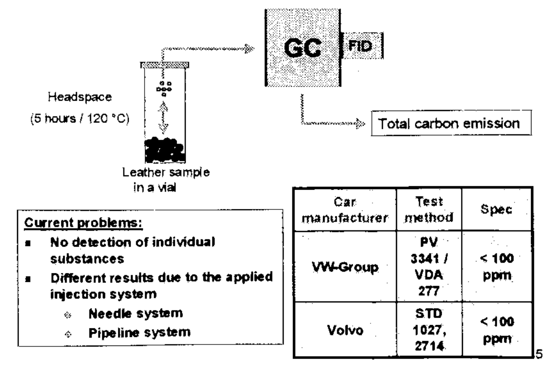

Figure 7. - Static headspace - test method and specifications

trolled. The principle of the method is shown in Figure 8. A small leather sample is placed in a glass tube, heated to 90°C to measure the VOC (volatile organic compounds) or to 120°C to measure the FOG (low volatile organic compounds). With helium or nitrogen gas the evaporated chemicals are carried from the leather sample in the desorption tube to a cryo-trap, in which they are concentrated at a temperature of -150°C. When the heating of the desorption tube is finished, the gas flow is stopped and the emittents, which are now completely in the cryo-trap, are immediately transferred to a gas chromatograph, where they are separated and subsequently detected by mass spectrometry.

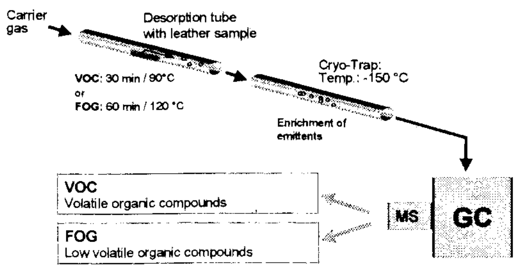

Figure 8. - Dynamic headspace - test method

With the dynamic headspace test two kinds of emittents are detected: moderate volatile organic compounds (VOC) and low volatile organic compounds (FOG). In contrast to the static headspace test, individual substances can be, as far as possible, identified besides the sum of emittents. These individual substances are automatically cross-checked with a list of toxic substances (carcinogenic, mutagenic or teratogenic) and marked, if identified in this list. Typical substances that are detected are shown in Table IV and V.

TABLE IV
Typical VOC Substances Detected with Dynamic Headspace Test

Typical Emittents*:	Formic acid
	Aldehydes
	NMP
	Phthalates
	Glycols
	Glycol ether
	Fatty acid methyl ester
	Fatty acids (<C18)
	Fatty alcohols
	Alkanes

*Emittents in the boiling range of n-alkanes C_7 to C_{20} (100°C to ~ 350°C)

It is important that the substances that are found by the dynamic headspace test are mainly brought into the leather during the wet-end process (fatliquoring, retannage and dyeing) and by finishing. Figure 9 shows the increase of total VOC and total FOG in comparison with the processing stage of a chrome tanned automotive leather.

TABLE V
Typical FOG Substances Detected With Dynamic Headspace Test

Typical Emittents*:	Fatty acids
	Fatty acid ester
	Fatty alcohols
	Phthalates
	Tributoxyethylphosphate
	Glycol ether
	Antioxidants
	Alkanes

*Emittents in the boiling range of n-alkanes C_{16} - C_{32} (> 250°C)

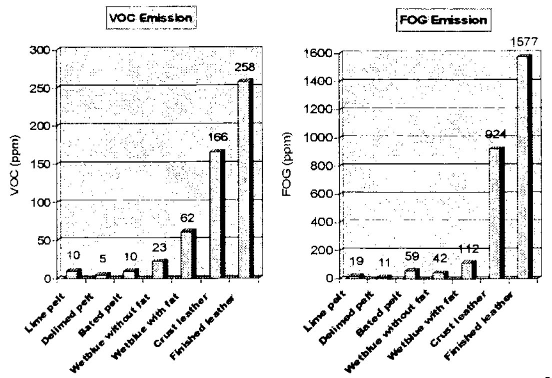

Figure 9. - Dynamic headspace chrome tanned automotive leather

In cooperation with a German automotive leather company, we have initiated an interlaboratory test to investigate the reproducibility of total VOC and FOG emission values and the detection of individual substances in several laboratories. To minimize errors, a piece of chrome tanned leather was grinded. Then we ordered tests from two institutes. One test result we received from a car manufacturer and a fourth one from our own laboratory. Table VI and VII show the central statement of the tests. For better clarity, some individual substances are combined in substance groups and all substances which are found with less than 10 ppm in VOC respectively 20 ppm FOG from all laboratories are summarized under the term "total individuals less than 10 ppm" respectively "total individuals less than 20 ppm".

The result of these interlaboratory tests provokes reasonable doubts. The determined values of VOC range from a total of 106 ppm up to 603 ppm. In FOG, they range from 345 ppm up to 4728 ppm. This is factor 6 to 13! The same considerable differences are shown in identifying the individual substances.

As a further investigation, we made our own trials on the

TABLE VI
Test Results Interlaboratory Test - VOC

Substance	Institute 1	Institute 2	Laboratory Boehme	Laboratory Car Manufacturer
formic acid		16		
N-methyl-pyrrolidine	59	56	45	28
2,4,7,9-Tetramethyl-5-decin-4,7-diol	8	11	31	26
2,6,10,14-Tetramethyl-Pentadecane= Pristan	20	25	64	21
Diisobutylphthalate		17		
Hexadecanol	11			3
Hexadecanoic acid		12		
Branched alkane	12			
Ölberg	460	162	237	
Alkanol/Alkene/Cycloalkane/...		62		2
Aliphatic		63		
Hydrocarbon			10	
Alcohol			14	
not clearly identifiable		13	6	2
total individuals over 10 ppm	570	437	407	82
total individual less than 10 ppm	33	89	45	24
overall total VOC	603	526	452	106

TABLE VII
Test Results Interlaboratory Test - FOG

Substance	Institute 1	Institute 2	Laboratory Boehme	Laboratory Car Manufacturer
Tetradecanoic acid		113	29	
Pentadecanoic acid		31		
Hexadecanol	62	82	127	46
9-Hexadecenoic acid		59	9	
Hexadecanoic acid		123	41	
9-Octadecene-1-ol	200		195	114
Octadecanol	48			20
Oleic acid methyl ester		32	53	
Octadecanoic acid		32		
Octadecanoic acid methyl ester			23	
Oleic acid		39	10	
Fatty acid amide		32		
Oleic acid amide		85		
2,2'-Methylen-bis(4-methyl-6-tert-butylphenol)	84	286	24	11
Bis(2-ethylhexyl)-phthalate = DEHP = DOP		44		
Ölberg	451	1059	1034	
Alkanol/Alkene/Cycloalkane/...		673		19
Aliphate		735		62
Hydrocarbons			23	
Alcohol			67	4
not clearly identifiable		1225	50	8
total individuals over 20 ppm	845	4650	1685	284
total individuals less 20 ppm	9	78	25	61
overall total FOG	854	4728	1710	345

uneven nature of leather by means of differences in the area. This idea arose when looking at the correlation of the sample size to the whole leather size. See Figure 10 which is self-explanatory.

Proportion: leather hide – test sample

Leather hide:
area: 5-6 m^2
weight: 3-4 kg
thickness: 1,2 mm

Test sample:
area: 1 mm^2
weight: 10 mg
thickness: 1,2 mm

	Leather hide	Test sample
area (mm^2)	5.500.000	1
weight (mg)	3.500.000	10
volume (mm^3)	6.600.000	1,2

Figure 10. - Dynamic Headspace - test sample

A hide was processed to ideal emission behavior. Then samples are taken as shown in Figure 11.

Sampling:

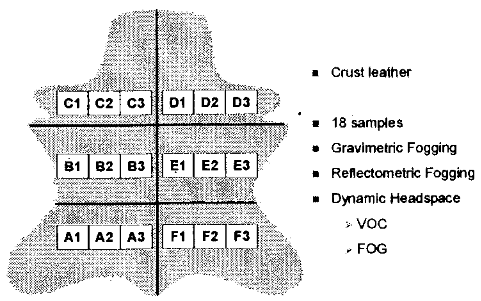

Figure 11. - Dynamic Headspace - A microscopic test method for the evaluation of a macroscopic area-measuremed material with natural grown structure

These samples have been tested in our laboratory and the results are shown in Table VIII.

As anticipated, the microscopic method dynamic headspace shows significant differences between the several leather areas, whereas more macroscopic methods like the fogging test is within the tolerance.

We found a difference between the neck (average of samples C and D) and the back (average of samples A and F) in VOC of approximately 50 ppm and in FOG of approx. 165 ppm. The total average VOC is approximately 80 ppm and the FOG is approximately 460 ppm. This means that the VOC and FOG differences between neck and back are approximately 35 - 60 % of the total averages! We want to point out that this result is currently based on two trials, one chrome tanned leather and one chrome-free leather. The concrete numbers differ, the overall statement is the same.

Conclusions

This paper summarized the current test methods concerning the emission behavior of automotive leather. It is not possible to concentrate only on one method to receive a reliable result of the real situation. The emission chamber test has the great advantage that larger pieces of leather can be tested, which gives a better reflection of the naturally grown and uneven material leather. But this method is extremely expensive, it is slow, complex and it is not possible to run it self-controlled. Therefore the emission chamber test is not suitable for routine quality tests.

It was shown that, on the other hand, the dynamic headspace test, which seems to be planned as a scale-down of the emission chamber, gives only limited informative results about the complex material leather. It is for sure an excellent method for totally homogeneous artificial materials. However, for naturally grown materials, where the applied chemicals have different affinity to the leather fiber, this method can only give semi-quantitative information. This was clearly shown in the very diverging results within the leather hide and between the test laboratories. As stated clearly in test method VDA 278, we also want to point out that the results of the dynamic headspace are not suited to estimate the real concentration of emittents in the car interior.

Acknowledgments

We acknowledge the company BADER for the cooperation with regard to the mentioned inter-laboratory test.

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TABLE VIII
Test Results Samples From Different Leather Areas

Sample	gravimetric Fogging 16h/100°C(mg)	reflectometric Fogging 6h/75°C(%)	VDA 278 VOC(ppm)	VDA 278 FOG(ppm)
A 1	0.4	97	60	429
A 2	0.3	96	38	314
A 3	0.3	97	44	404
B 1	0.2	97	76	482
B 2	0.3	98	124	540
B 3	0.3	95	102	485
C 1	0.3	97	122	624
C 2	0.6	95	154	718
C 3	0.7	97	114	569
D 1	0.5	97	75	423
D 2	0.5	98	78	459
D 3	0.5	95	94	540
E 1	0.3	95	62	384
E 2	0.3	96	57	336
E 3	0.4	97	73	434
F 1	0.4	95	62	424
F 2	0.4	96	43	328
F 3	0.5	96	56	444
Average Value Back Pieces A1, 2, 3, F1, 2, 3	0.4	96	51	391
Average Value Neck Pieces C1, 2, 3, D1, 2, 3	0.5	97	106	555
Average Value All Pieces A1 - F3	0.4	96	80	463

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Convention Discussion

Rodney Hammond, Seton Company - The variability is actually sometimes greater than the specification limit. For a natural material like leather, I guess that is not unusual but what do you think the future trends are going to be from the car industry on such things as headspace emissions on the different things that you were talking about?

I hope very much that not only the chemical industry will do trials as I have presented now, but also the test institutes and the automotive industry. Then the car industry can be convinced to come back again to tests that really reflect the naturally grown material leather. And there won't be so many problems with the sampling of the uneven nature of leather. In the past years, there was the tendency to more and more microscopic tests. For the material leather, this is not the right way. So I do have the hope that the car industry can be convinced to come back to more serious leather test methods.