

Fogging for automotive leathers - the new EN 14288/ISO 17071 test method.

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Introduction

One of the key emission tests that leather is required to undergo by the automotive industry is its propensity to fogging, that is, the ability when heated to emit substances that form a haze-like layer on the windscreen of a car. Naturally the automotive industry requires that the interior materials of a car do not exhibit this fogging effect to any significant effect.

Until now the German DIN 75201 test method adopted in 1992 has been the standard reference for many supplying leather to the European automotive industry. Variations on this method have been used by other non-European automotive manufacturers.

In December 2003 the European Committee for Standardization, CEN, released for leather a new European Standard test method for the determination of fogging characteristics. This Standard test method is EN 14288 **Leather – Physical and mechanical tests – Determination of fogging characteristics**. This test method is currently in the process of being also adopted as an ISO Standard, namely ISO 17071.

With the new EN method the limits of the reflectometric procedure are clearly indicated and there are some practical changes in the test parameters when compared with the DIN procedure. The new EN method more closely reflects that which is being used in many tannery test laboratories.

A study has been undertaken to evaluate the influence of the new parameters on the test results for automotive leathers. A further study has been made to compare several of the differing test methods used internationally.

The results and their implications for the automotive leather suppliers are presented.

It is well documented over the last years which leather processes and which chemicals influence the degree of fogging that occurs, so this aspect is not part of this presentation.

New, highly sophisticated methods for measuring and analysing the emissions from automotive interior trim materials are starting to be requested by some car manufacturers¹. Typically these tests are made using gas chromatographic head space techniques and typically involve extremely small samples (e.g. 10 mg!) and temperatures in the range 90 – 120°C. No doubt these new procedures will develop further but the basic standard for the tannery remains the traditional fogging test method.

Background

With a large amount of work the German Standard, DIN 75201, was published in 1992 as the definitive method for measuring fogging of automotive interior trim materials. The DIN

75201 method is actually 2 completely separate test procedures, which were unfortunately mixed together in the one Standard.

- Method A is the so-called reflectometric method that measured the opaqueness of the fogging layer on a cold glass surface.
- Method B, the gravimetric method, measured the quantity of condensate that formed on a cold surface.

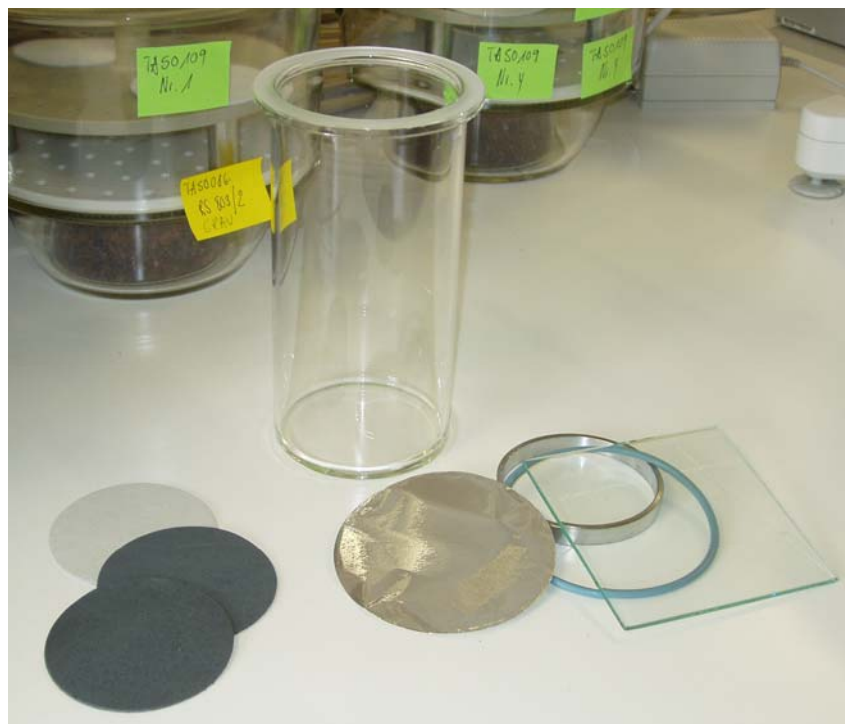
The results obtained from Method A and Method B have been found to have no relationship with one another as they are measuring different parameters.

Why was there a need for a new method?

Over the last 10 years it was quite noticeable that different test houses were obtaining considerably different results for one of the 2 methods, namely the reflectometric method. Additionally for very practical reasons many suppliers of automotive leather were not following precisely the DIN 75201 procedures and had introduced their own variations to the methods. In the present times to hold a production lot for up to 10 days to await a quality test result is economically impossible.

The DIN Standard incorporated 2 quite different test procedures but they were not separated in the text. So it was difficult to clearly follow one or the other method on its own. Over time it was obvious some additional explanations to the methods were necessary.

It was necessary to evaluate the significance of these aspects and if they could be incorporated into a new Standard.



What is the fogging test as in EN 14288 and DIN 75201?

The standard procedure for testing the propensity to cause fogging involves cutting an 80mm diameter circular sample of leather and removing absorbed water by drying over a desiccant. This sample is then placed at the bottom of a tall glass beaker, which is immersed in an oil bath heated at 100°C. The top cover of the beaker is cooled at 21°C to allow the substances emitted from the leather sample to condense on the cool surface. In the case of the reflectometric method a glass plate (at 21°C) covers the heated beaker for 3 hours. The glass plate is removed and after conditioning the opaqueness of the condensate is measured with a reflectometer.

For the gravimetric method the top of the heated beaker is covered with a pre-weighed aluminium foil (at 21°C) for 16 hours. The aluminium foil is removed and dried over a desiccant for 4 hours before re-weighing.

Are there other procedures other than the DIN method?

Yes. As is common in the automotive industry, different car manufacturers have introduced their own variations of this procedure. Some specify heating the sample less, for example only to 85°C or 90°C, and cooling the glass plate less, for example to 38°C. These parameters give quite different results when compared with the DIN procedure. Hence it is extremely important that the test method parameters are presented along with the results obtained.

Discussion

1) Why is the reflectometric method less used?

It has been very noticeable that the inter-laboratory variations in results for Process A, the reflectometric method, have resulted in many of the European automotive manufacturers now only specifying the much more consistent Process B, gravimetric method.

A well reported inter-laboratory trial² using results from 7 test laboratories confirmed this variation. The results were as follows:

Method A: Reflectometric

	mean reflectance value(%)	standard deviation
Crust leather	47	17
Finished leather	74	25

Method B: Gravimetric

	mean gravimetric value(mg)	standard deviation
Crust leather	3.27	0.95
Finished leather	7.27	1.28

Various additional round-trials were undertaken to try and identify the reason for the variability in Process A. Variations in drying agents, temperature of the oil bath and cleanliness of the glass plates did not result in an improvement in the inter-laboratory agreement.

For the reflectometric method the automotive manufacturers typically set specifications in the range of 60% to 90%. As shown above the inter-laboratory confidence interval for this range is quite large, approx. 25, such that a definite compliance with the specifications is almost impossible to ascertain. Even if the repeat testing within the one laboratory show very good agreement, it is the testing between laboratories that is the critical variance where problems occur.

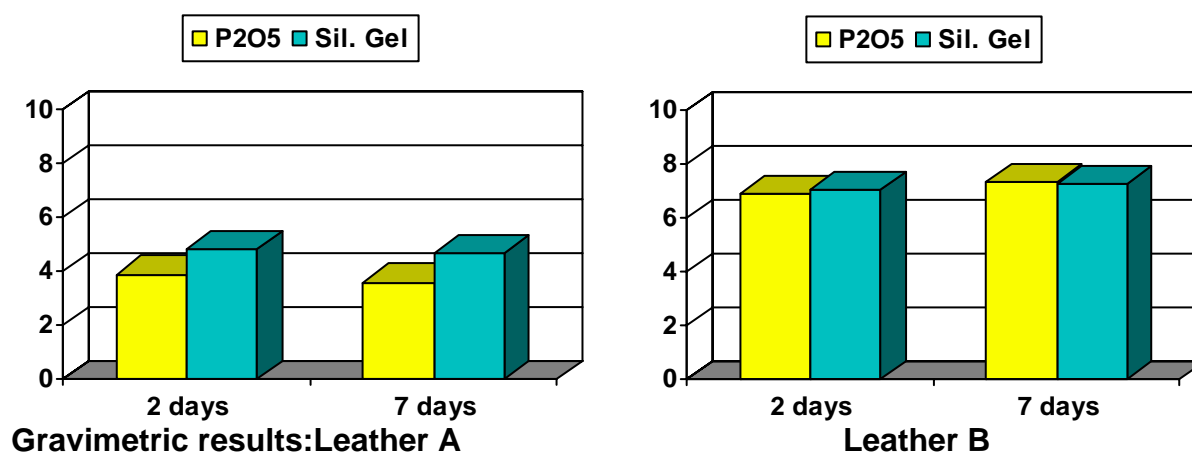
For the gravimetric method the requirements from the automotive manufacturers vary from less than 3.0 mg up to less than 7.0 mg. In this range one can conclude an inter-laboratory confidence for the test results of the order of 1.0 mg is typical.

Further, the new EN 14288 test method now clearly separates the 2 procedures into Method A and Method B. The new Standard informs the user that there is no mathematical correlation between the results obtained for the 2 methods. Further, importantly it clearly explains that the reflectometric Method A has high variability in results.

2) Using alternative drying agents

The leather samples are required in DIN 75201 to be dried using the drying agent phosphorous pentoxide, P_2O_5 . This chemical has handling problems especially for staff not well trained in the use of chemicals. P_2O_5 combines with moisture to form a very corrosive acid. Further, once the surface of the chemical is wet from absorbed moisture, this layer blocks the underlying P_2O_5 from absorbing further moisture. Reusable silica gel is commonly used as a laboratory drying agent and many tanneries have adopted it for the fogging test.

Comparison of the gravimetric values of leather samples dried over 2 different drying agents confirmed for tannery test laboratories, that while the phosphorous pentoxide gave the lowest results, for production QC purposes in many cases a 2 day drying over reusable silica gel was capable of giving results within the specification. Results for 2 leather samples are shown below, they are representative of results from many leather samples.



Gravimetric fogging results (mg)

mean value after 2 days mean value after 7 days

Leather A

Phosphorous pentoxide	3.9 mg	3.6 mg
Reusable silica gel	4.8 mg	4.7 mg

Leather B

Phosphorous pentoxide	6.9 mg	7.3 mg
Reusable silica gel	7.1 mg	7.2 mg

The new EN 14288 test method still recommends phosphorous pentoxide as the drying agent but importantly it allows for the use of alternative drying agents when they give equivalent results. This reflects the situation which is being practised by much of the industry, both in the tanneries and by automotive companies.

3) Are long drying times necessary?

The long drying time prior to testing required for items made of natural products, such as leather, has been a big problem for tanners. A 7 day drying time before even starting to carry out the test is in most cases not economically possible today.

A series of different leather samples were dried over 2 different desiccants; namely phosphorous pentoxide and reusable silica gel. The weight loss after 2 days and 7 days was measured.

Leather weight loss (%)

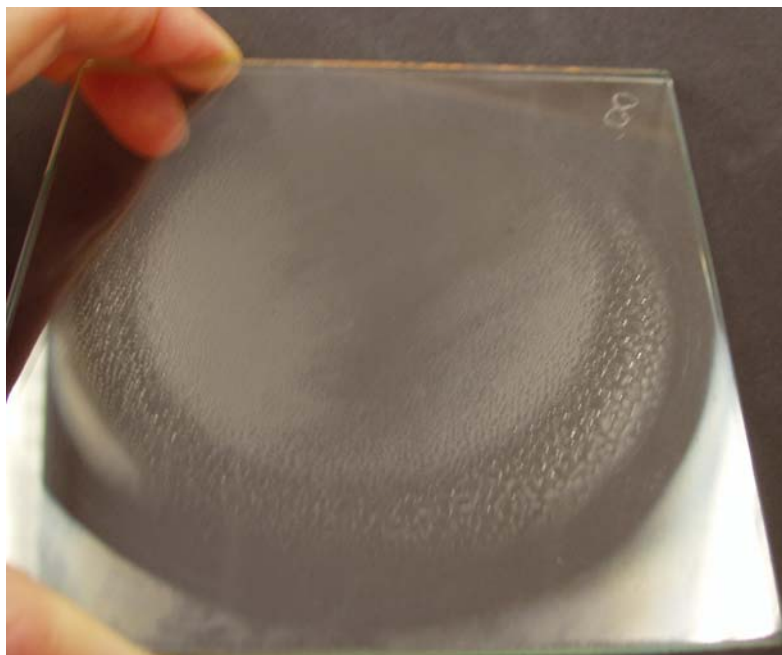
	Weight loss after 2 days	Weight loss after 7 days
Phosphorous pentoxide	2.8%	5.3%
Reusable silica gel	4.6%	6.5%

So taking into account the ease of handling and reusability, the results clearly support the use of reusable silica gel as the desiccant of preference for use in tannery test laboratories. This drying agent removes moisture quickly allowing a prompt testing of the leather.

The new EN 14288 test method recognises the economical constraints of production and allows the use of 2 days for the drying of samples. A repeat using the traditional 7 days is offered in cases when a sample fails to meet the customer's specifications.

4) Interpretation of the fogging condensate

The reflectometric Method A is only valid for those condensates that form fine "fog-like" particles spread relatively evenly over the glass surface. Often larger transparent droplets and films can form (see photo below); in this case the method reports them with as having little reflection, implying a good result, when the truth is that the results are very bad. A visual evaluation of the condensate is important. It is clear from many "unusual" test results seen that in many cases this aspect is overlooked and the glass plate reflection value is simply measured regardless of the condensate type.



The new EN 14288 test method requires a visual assessment of the condensate and if it is a transparent film or similar then the test procedure is stopped at this point, as the reflectometric method is not able to give meaningful results.

5) What influence do different test parameters have on the result?

The SAE J1756 test method for fogging has various options for heating the sample and the temperature of the cooling surface.

An evaluation of the differences between the EN 14288 / DIN 75201 Method A conditions of 3 h heating at 100°C and 21°C condensate cooling and the commonly used SAE J1756 test method option with 6 h heating at 85°C and 38°C condensate cooling was undertaken. The reflectometric results taken after 1 h conditioning were as follows:

Sample No.	EN 14288 (7 d. drying)	SAE J1756 (7 d. drying)	SAE J1756 (no drying)
1	21%	88%	90%
2	59%	87%	86%
3	50%	86%	86%

For this SAE J1756 method, the lower heating temperature of the leather sample and the higher temperature of the cooling glass plate combine to give considerably higher reflectometric values. Additionally, the SAE method is clearly not sensitive in differentiating between leather samples when compared with the EN 14288 / DIN 75201 procedure. In fact the reflectometric results using this option of the SAE method do not vary even if the leather test sample is not dried prior to testing!

Therefore it is clear that the test parameters are very important and as indicated here it is extremely difficult to compare results for different car manufacturers as most have different test parameters.

Summary

While the new EN 14288 Standard retains the basic elements of the traditional DIN 75201 Standard, it has been introduced to update the procedures and agree better with the practices being carried out by the industry. It takes into account the economic needs of tanners and still give results which can be used with confidence to meet customer's specifications.

The EN 14288 Standard is currently in process of also being introduced as an ISO Standard, namely ISO 17071.

References

1. H. Schulz, Leder & Häute Markt, March 2002, p. 25 – 34.
2. VGCT Commission/TEGEWA, Leather International, Aug. 2000, p. 44-46.