2001-01-0933

New Catalyst Preparation Procedure for OBDII-Monitoring Requirements

Margret M. Schmidt
Shell Global Solutions

Michael J. Brady, Craig Summers
DaimlerChrysler

Meike Reizig, Rolf Brück, Jürgen Breuer
Emitec GmbH

ABSTRACT

In order to match catalyst OBDII conditions the common procedure is oven aging with air, which is not suitable for complete converter systems due to mantle corrosion. The goal was, therefore, to find an alternative procedure to ensure a defined catalyst aging that would match 1,75 times the emission standard and is also good for SULEV.

The new procedure currently being developed allows the aging of metal and ceramic catalysts as well as complete catalyst systems. The paper will present the aging process, emission data of fresh and aged catalysts and the feedback to the test car OBDII system.

INTRODUCTION

Since the introduction of the 1994 model year for passenger vehicles automobile manufacturers have been introducing diagnostic systems in order to determine – amongst other things – excessive exhaust gas emissions. The legislation in the United States distinguishes between two regulations, OBD (On Board Diagnostics for 49 states) and OBD II (On Board Diagnostics II for California).

Monitoring the efficiency of catalysts means that in the case of a malfunction the Malfunction Indicator Light (MIL) in the vehicle is illuminated and the driver thus informed about the malfunctioning catalyst. Until now, the malfunction of catalysts has only been specified by means of HC emissions. In California, for example, the specification for Low Emission Vehicles (such as TLEV, LEV and ULEV vehicles) stated that the malfunction must be recognised whenever 1) tailpipe HC emissions exceed 1.75 times the applicable NMHC standard or 2) the NMHC conversion efficiency of the monitored portion of the catalyst system falls below a level of 50% (1).

In a 5-year transitional phase starting in 1998, less stringent criteria were applied by the California Air Resources Board (CARB): 2.0 times the standard plus the 4K mile baseline for TLEVs, 2.5 times the standard plus the 4K mile baseline for LEVs, and 3.0 times the standard plus the 4K mile baseline for ULEVs (2).

In the meantime, manufacturers have successfully been able to comply with the 1.75 times ULEV HC Standard using the available diagnostic systems.

Many results have demonstrated that NOx emissions cannot be compared with the deterioration of the catalyst – with regard to HC emissions. This is why - from model year 2004 onwards - limit values in the LEV II program will be extended as follows: 1) hydrocarbon (HC) or nitrogen oxide (NOx) emissions exceed 1.75 times the applicable FTP emission standard, or 2) the Average Federal Test procedure (FTP) for Non-Methane Hydrocarbon (NMHC) or NOx conversion efficiency of the monitored portion of the catalyst system falls below a level of 50% (3).

In this paper, however, only the LEV I and not the LEV II legislation, will be discussed.

In order to represent aging of the catalyst with its related reductions in efficiency and oxygen storage capacity, manufacturers apply a range of aging methods.

These methods include:

- oven aging (e.g. with air or hydro-thermal).
- aging by means of misfires on a motor test bench, on a chassis dynamometer (CD) or on the road,
- aging on a motor test bench via cyclical alteration of the air/fuel ratio and/or air injection and intended poisoning (3).

The efficiency of the catalyst referring to the emitted HC value is at the moment primarily determined via the OSC (Oxygen Storage Capacity) of the coating. A Lambda probe is therefore installed before and after the three-way catalyst in the exhaust gas pipe. The probe after the catalyst receives a reduced or belated signal. By means of a relative comparison of the two probe signals the OSC of the catalyst is determined, which then allows a forecast with regard to the HC conversion rate. (4)

Another method to monitoring the efficiency of the catalyst can be carried out using sensors, which measure the temperature in the catalyst, and the resultant ΔT signals. However, this method is not discussed in this paper.[5]

It should also be mentioned that test bench aging processes (by means of misfires, for example,) may involve the risk of mechanically destroying the catalyst's substrate. In the following text, a new oven aging method is presented with the advantage that it can be utilized for any catalyst substrate and that even canned subsystems can be heat treated in the oven. The catalyst's substrate therefore does not have to be disassembled.

A major advantage of this method is that the catalyst can be tested on the test bench (roller type or motor) when brand new and after 4 K miles, aging takes places (without the risk of mechanically destroying the component) and the aged component can be re-measured after treatment. Subsequent aging can also be easily shown using this method.

OVEN AGING METHODS

COMPARISON OF METHODS

The comparison in table 1 shows that oven aging at high temperatures is the most cost efficient and fastest method for substrate aging. The disadvantage for metal substrates under these thermodynamic conditions is the oxidation behaviour of the mantle and foil materials. By using appropriate special mantle materials this behaviour could be counterbalanced. Canned metal or ceramic substrates can, however, never be aged under these conditions.

Table 1: Temperature Aging Processes

	Time / Costs	Metal Substrates	Ceramic Substrates
Vehicle	- -	+	+
Engine Test Bench	-	+	+
Oven Aging at low Temperature	+	+	+
Oven Aging at 1200-1300°C	++	-	+
Aging under hydrothermal Conditions	+	+	+

VACUUM OVEN AGING METHOD

Several criteria had to be met in the development of the new oven aging method:

- time
- costs
- reproducibility
- aging of canned substrates
- correlation with regard to the aging process in the vehicle

Vacuum oven aging can be carried out at temperatures ranging from 1,000 to 1,330°C and over a time period of < 1h to < 50h. The vacuum is a high vacuum of < 10^{-4} mbar.

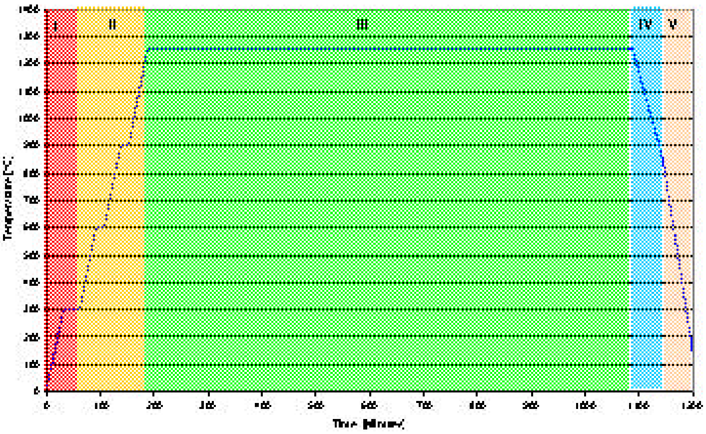

Fig. 1: Process of oven aging

Phase I: convectional heating in a vacuum with up to 300°C (holding time 30 minutes) incl. argon flushing

Phase II: heating in 300°C stages and holding periods of 15 minutes

Phase III: aging at, e.g., T = 1,250°C for 15h

Phase IV: vacuum cooling down to 850°C

Phase V: addition of argon/hydrogen mixture (5%) cooling down to 80°C

Aging in an oven is primarily a function of temperature and holding time.

TEST DESCRIPTION AND TESTING

Preliminary Testing

In preliminary tests the Light-Off (LO) behaviour of different coatings was measured using a synthetic gas test bench. The sample was subjected to air, which was mixed with 1,000 ppm propene and heated slowly. The HC concentration before and after the catalyst was measured by means of an FID.

The three sample substrates presented below were tested on the test bench in a fresh as well as aged condition (30 hrs. at 1,250°C at high vacuum). Substrates were coated as follows:

- Coating A = Tri-metal (1:14:1)
- Coating B = Pd/Rh (12:1)
- Coating C = Pd/Rh (5:1)

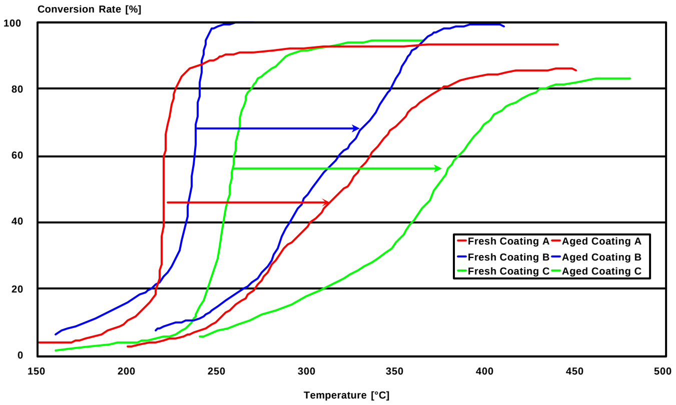

Fig. 2: Light-Off deterioation

Figure 2 shows that aging is not only a function of temperature and time but depends greatly on the composition of the coating.

The test results shows increased Light-Off temperatures T_{50} of 80-120K.

On an engine test bench the influence of vacuum aging on the oxygen storage capacity of the coating was examined. The examined substrate had coating B and was tested in a fresh as well as an aged condition (30 hrs. at 1,250°C at high vacuum). The engine used for testing was not the original engine but one that was available on the test bench.

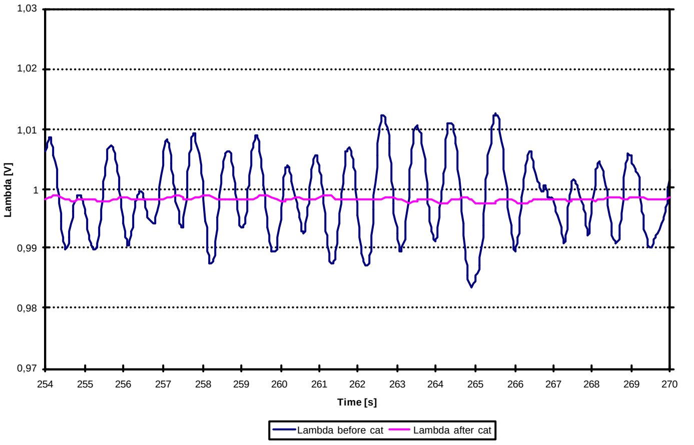

Fig. 3: Lambda measurement on a engine test bench from fresh CC with Coating B

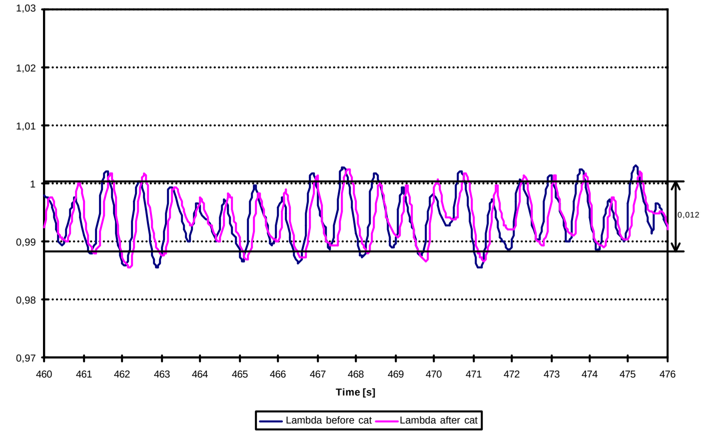

Fig. 4: Lambda measurement on a engine test bench from aged CC with Coating B

Figures 3 and 4 clearly show that aging under high temperature in vacuum has a very strong influence on the oxygen storage capacity of the coating similar to aging in air without damaging the mantle or foil material. In view of the very strong deterioration the aging of the coating should also be detectable in the vehicle by means of Lambda probe monitoring.

It is well known that the aging behaviour differs from coating to coating. Sample tests and information on the kinds of precious metal in the coating only permit a preliminary estimation of the aging temperature and the aging time. After test measurement, aging cycles will have to be modified and re-aged.

Aging of catalyst substrates

The preliminary tests gave some indication of the extent of substrate aging needed to produce the required deterioration of emission values in an FTP test. Therefore the following aged substrates were used for the FTP test:

- Set 1: fresh
- Set 2: 1290°C / 30h
- Set 3: 1310°C / 30h
- Set 4: 1330°C / 15h
- Set 5: 1330°C / 30h
- Set 6: 1330°C / 50h

Use in passenger cars

The passenger car used for tests on the chassis dynamometer was a Chrysler 300M, model year 2000. This vehicle was chosen since a diagnostic system had already been installed for OBD II. It had also been approved by the CARB. The vehicle was one of the mass produced series.

The catalyst converter in the vehicle is a two-pipe 1 brick installation, which means that the LEV limit value would have to be exceeded by a factor of 1.75 in order to make a valuable statement with regard to OBD compatibility.

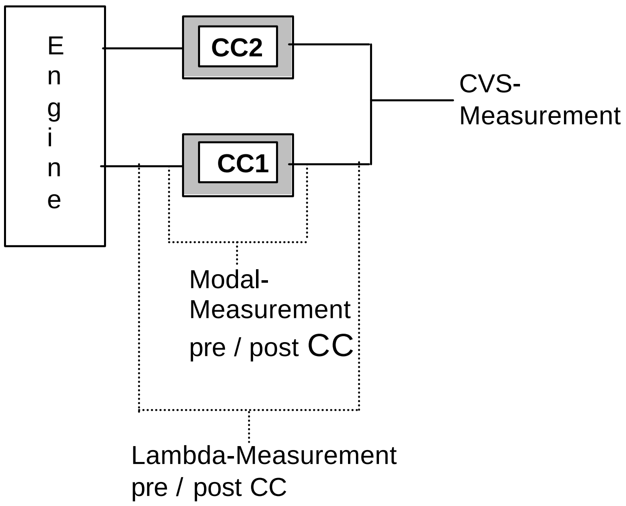

Fig. 5: Structure of the measurement

The substrates used had the dimensions ∅98.5 x 158mm, 600 cpsi and 0.03mm foil thickness. The coating used was Pd/Rh (12/1). During the test, either parallel modal/bag measurements or a pure bag measurement was conducted.

Influence of the oxygen storage capacity

In order to compare the substrates aged under a vacuum with those aged on the motor test bench or in actual operation, the oxygen storage capacity of the aged coating and the reduction in efficiency of the coating have to show a clear and equal correlation.

There are three cases to be distinguished:

1. The HC emissions lie above the limit value, the MIL is not switched on → There is no correlation in the aging behaviour since the Lambda probes are not triggered - i.e., the oxygen storage capacity of the coating is still too good.

2. The HC emissions lie below the limit value, the MIL is switched on → There is no correlation in the aging behaviour since the oxygen storage capacity is worse in comparison to the efficiency of the precious metals.

3. The HC emissions are at the limit value, the MIL is switched on at the right point in time → There is a clear correlation between aging behaviour and methods applied.

Test Equipment

- The tests were carried out on a AVL Zoellner 40” compact chassis dynamometer with speed synchronised cooling fan at ambient conditions. Load was applied at v_{const} by a computer controlled electric throttle actuator.

- The emission measurements (both standard CVS tests and modal measurements) were carried out with a Horiba CVS and mexa-analysers of the 9000 series. A Siemens CATS system was used as control unit and data logger for CD related data such as speed, load, temperature etc., as well as for all emission data.

- The data from the OBD II was recorded on a DRB III diagnose computer (DaimlerChrysler Corporation)

- During the test cycles 2 Lambda log sensors (separate from original Lambda sensors) traced the Lambda signal pre / post catalyst

Test operations

The agreed emission test series for each catalyst set consists of the following sequence:

FTP75 → 300km mileage accumulation → FTP75

The 300km mileage accumulation was driven at a definite speed order up to 80 km/h on the chassis dynamometer. The mileage accumulation was conducted to prove the constancy of aging, e.g. whether reactivation of the precious metals or improvements in the oxygen storage capacity could be observed.

At the end of mileage accumulation modal emission measurements and Lambda measurements at different constant speeds (50, 80 and 100 km/h) were built in.

Test Fuel

Shell Optimax (top tier Shell gasoline) was used during the entire test program.

Test results

The limit value of the test LEV test car for 100,000 miles for HC emissions in the FTP test amounts to 0.09 g/m. The limit value increased by the factor of 1.75 where the MIL would have to switch on is 0.1575 g/m.

In the following we examine the cold start behaviour of a fresh, a slightly aged and a highly aged substrate.

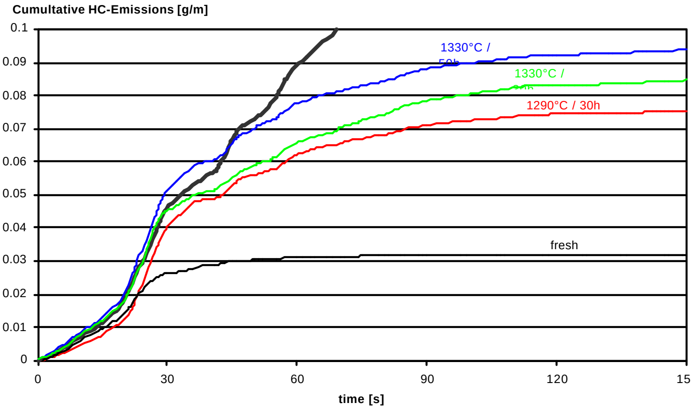

Fig. 6: Cold start behavior from fresh and aged CC.

As early as in the first 150 seconds, temperature as well as time-related dependencies of oven aging become visible. To ensure that the MIL is actually triggered in the vehicle, the reduced oxygen storage capacity must be matched by the efficiency of the precious metals.

To be able to measure the oxygen storage capacity, three constant load points (50, 80 and 100 km/h) were used in accordance with the FTP test and in each case the Lambda value was measured both before and after the catalyst. The following four graphs show the oxygen storage capacity at a constant speed of 50 km/h for the fresh as well as for the three aged substrates (1,290°C / 30h; 1,330°C / 30h; 1,330°C / 50h). The reduction in oxygen storage capacity is clearly visible dependent on the aging stage of the catalyst.

On the basis of the measured values, a strong increase in the amplitude becomes visible given increased aging.

Since this reduced oxygen storage capacity clearly correlates with the measured HC (table2) deterioration and since the MIL in the vehicle was triggered, this aging method is very much in line with aging under real conditions.

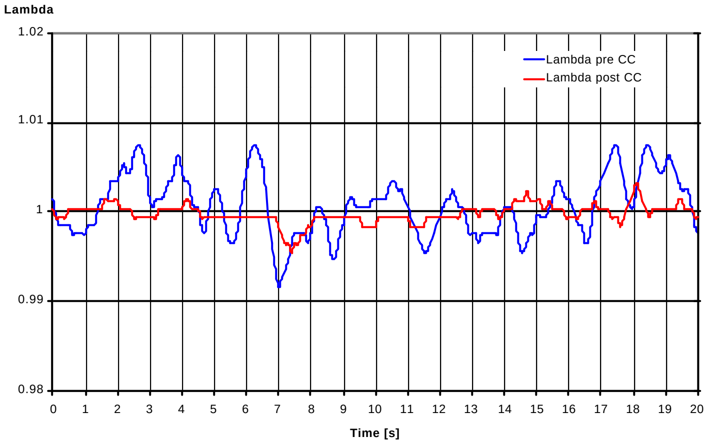

Fig. 7: Lambda pre / post fresh CC at constant speed (50km/h)

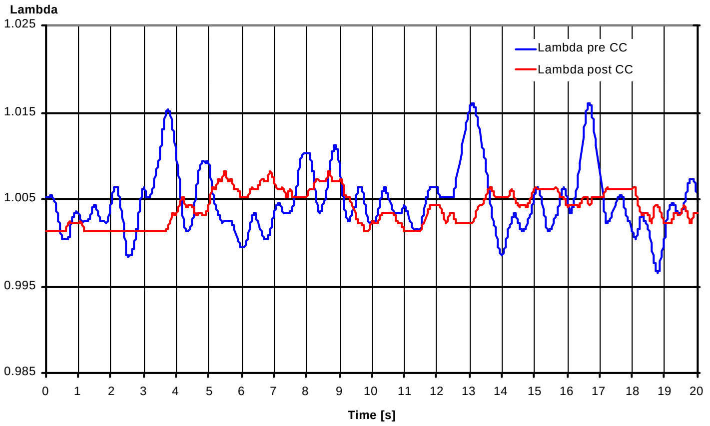

Fig. 8: Lambda pre / post aged (1290°C / 30h) CC at constant speed (50km/h)

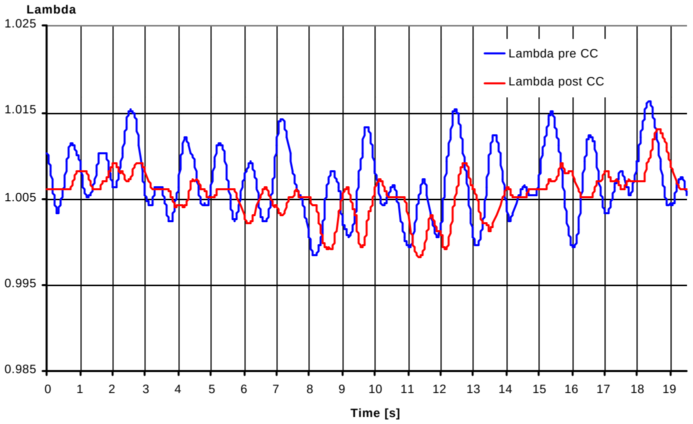

Fig. 9: Lambda pre / post aged (1330°C / 30h) CC at constant speed (50km/h)

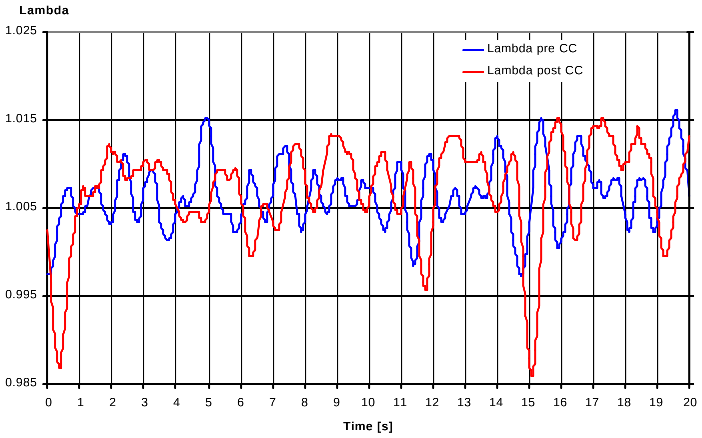

Fig. 10: Lambda pre / post aged (1330°C / 50h) CC at constant speed (50km/h)

The following table shows an overview of test results:

Table 2: Overview of the CVS-results

Aging conditions	THC [g/m]	CO [g/m]	NOx [g/m]	MIL
Fresh	0.043	0.279	0.104	No
Fresh	0.023	0.086	0.112	No
30h / 1290°C	0.131	1.062	0.532	No
30h / 1290°C	0.146	1.261	0.500	No
30h / 1310°C	**0.158**	1.906	1.000	R
30h / 1310°C	0.149	1.589	0.675	No
15h / 1330°C	0.153	1.624	0.776	No
15h / 1330°C	**0.160**	1.611	0.847	R
30h / 1330°C	**0.168**	2.864	1.071	L+R
30h / 1330°C	**0.180**	2.872	0.901	L+R
50h / 1330°C	**0.178**	2.911	1.046	L+R
50h / 1330°C	**0.167**	2.854	0.961	L+R
Fresh	0.039	0.289	0.064	No

... no MIL is switched on ...
L,R – yes, MIL switched on (reading of DRB III indicates left or/and right catalyst)

Test Comparisons

In addition substrates were aged for an EU3 passenger vehicle in order to show the correlations with European OBD standards. Unlike the EPA standard, in Europe a limit value increased by a factor of 2 would have to be monitored (limit value = 0.17g/km = 100%).

In order to achieve the relevant limit values for this project, three identical substrates were aged in several stages.

The results of the emissions are presented in Figure 11.

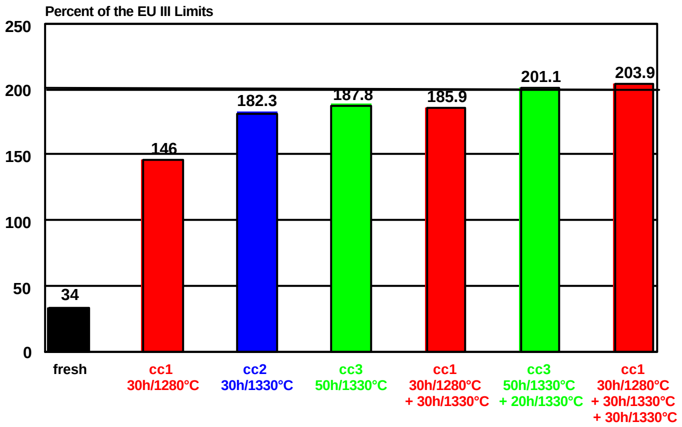

Fig.11: HC-Emissions of different aged EU3 CC for a V8-Engine

Catalyst 2 was not aged to 200% since it had been used directly by the customer for OBD adjustment purposes. Catalysts 1 + 3 were re-aged until the limit value of 200% was achieved. In both cases it was possible to present such a system very well.

CONCLUSION

The tests on the synthetic gas test bench, the engine test bench and with a vehicle on chassis dynamometer proved that catalyst substrates can be aged in a reproducible fashion under a high vacuum and is in line with the aging behaviour on the vehicle. From the tests we can conclude the following:

- The Light-Off temperature T_{50} (50% conversion rate) increased of 80-150 K.
- Reduced oxygen storage capacity of coating depended on aging temperatures and times.
- The reduction of the oxygen storage capacity and the reduced efficiency of the precious metals correlates very well with the aging behaviour in the vehicle.
- The method is cost-efficient (several substrates at the same time as well as canned systems can be aged).
- Canned systems can be re-aged.
- NOx emissions also worsened which means that this method is not only to be used for the application of OBD with regard to HC (LEV I) but also for NOx (LEV II).

In the future, the aging method under a high vacuum might increase the availability of aged substrates for OBDII applications. It is a very simple method of presenting the substrates required for the relevant approval procedures.

REFERENCES

1. CARB Mail-Out#94-38, October 11, 1994
2. CARB Mail-Out#96-34, October 15, 1996
3. CARB Mail-Out#99-12, May 26, 1999
4. Jeffrey Hepburn, Timothy Chanko, JoAnne McKenzie, Robert Jerger, and Douglas Dobson “OBD-II Threshold Catalyst Aging Process”, SAE Paper 972853
5. Stephan Pelters, Dietmar Schwarzenthal Porsche AG; Wolfgang Maus, Helmut Swars, Rolf Brück Emitec GmbH; “Alternative Technologies for Studying Catalyst Behavior to Meet OBD II Requirements”, SAE Paper 932854