SAE TECHNICAL
PAPER SERIES

2003-01-3753
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FILIADA À SAE INTERNATIONAL

SAE BRASIL

Congresso 2003 SAE BRASIL

**12º Congresso e Exposição Internacionais
de Tecnologia da Mobilidade
São Paulo, Brasil
18 a 20 de novembro de 2003**

AV. PAULISTA, 2073 - HORSA II - CJ. 2001 - CEP 01311-940 - SÃO PAULO - SP

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ABSTRACT

The modern Diesel engine is one of the most versatile power sources available for mobile applications. The high fuel economy and torque of the Diesel engine has long resulted in global application for heavy-duty applications. Moreover, the high power and excellent driveability of today's turbo-charged small high-speed Diesel engines, coupled with their low CO_2 emissions, has resulted in an increasing demand for Diesel powered light-duty vehicles.

However, the demand for Diesel vehicles can only be realised if their exhaust emissions meet the increasingly stringent emissions legislation being introduced around the world. In the USA, light-duty Diesel (LDD) vehicles will have to meet the same emissions legislation as gasoline vehicles from 2004 onwards, while in Europe a similar target is expected when European Stage 5 legislation is introduced. In practice, such targets mean very high reductions (up to 90%) of nitrogen oxides (NOx) and particulate matter (PM) emissions may be required from today's levels. Drastically reduced NOx and PM emissions from heavy-duty Diesel (HDD) engines are also required in Europe and the USA in a similar time frame.

This paper reviews the developments in Diesel exhaust emissions control devices. The application of Diesel oxidation catalysts, particulate filters, and NOx control catalysts (NOx adsorber catalysts and Selective Catalytic Reduction systems) to help meet both light- and heavy-duty legislation is discussed. An overview of likely catalyst system designs to achieve high levels of PM and NOx conversion is given.

INTRODUCTION

Future legislation around the world for Diesel vehicles is becoming increasingly stringent, with the emphasis placed on lower PM and NOx emissions. Advances in engine design and control has shown, and continues to show, significant reductions in emissions. At the same time further advances in the high torque and excellent driveability of the Diesel engine has fuelled expansion of the Diesel sector.

To help achieve the tighter emissions requirements, advanced aftertreatment technology from oxidation catalysts to systems capable of high conversion of all four pollutants is being developed.

For passenger cars in Europe, Stage 4 legislation will be introduced in 2005, with significantly lower emissions limits than the currently applied Stage 3 legislation (Table 1). For Stage 4, NOx and PM emissions have been halved from the Stage 3 limits, while CO and HC emissions require more moderate reductions. In addition, the durability requirement over which the emission standards have to be met has increased from 80,000 km for Stage 3 to 100,000 km for Stage 4.

While LDD Stage 5 has yet to be set, it is widely expected that a further reduction of NOx and PM limits will occur, to give emissions levels comparable to those required from gasoline cars (0.08 g/km NOx in Stage 4), and similar to the standards already set in the USA.

Future USA legislation for LDD vehicles also focuses on NOx and PM emissions. For passenger vehicles, Tier 2 limits phase in between 2004 and 2007 with the limits for Diesel vehicles being the same as gasoline-powered vehicles. By 2007, the fleet average NOx emissions must meet 0.07 g/mile for all passenger vehicles up to 8500 lb. Within Tier 2, there are a number of emissions levels (bins) which vehicles can be certified to – the 0.07 g/mile fleet average NOx value occurs in bin 5 (Table 2). The emissions must be durable over 120,000 miles.

Emissions legislation for HDD engines in Europe is also forcing lower NOx and PM emissions. Table 3 shows the emissions limits for the European steady-state cycle (ESC) test procedure. Stage 4 (commencing in 2005) has a significant drop in PM and a more moderate NOx decrease. Stage 5 (commencing in 2008) introduces a further drop in NOx.

The steady decrease of NOx emissions for HDD engine legislation in Europe is in contrast to that in the USA. In the 2007 – 2010 timeframe, the NOx and PM emissions for HDD engines in the US are reduced ten-fold from the 2004 limits

(Table 4). The PM legislation is effective immediately in 2007, while the NOx and NMHC limits will be gradually phased in between 2007 and 2010. In addition, not-to-exceed limits of 150% of the legislation have been set, and these apply to a large proportion of the engine map in an effort to ensure high levels of emission control occur under a whole range of driving conditions. The emissions have to be durable for up to 435,000 miles.

Table 1: European LDD emissions legislation (g/km).

Stage (Year)	*CO*	*HC+NOx*	*NOx*	*PM*
3 (2000)	0.64	0.56	0.5	0.05
4 (2005)	0.5	0.3	0.25	0.025

Table 2: USA Tier 2 LDD emissions legislation (g/mile) to be phased in from 2004.

Bin	*CO*	*NMOG*	*NOx*	*PM*
8	4.2	0.125	0.2	0.02
7	4.2	0.09	0.15	0.02
6	4.2	0.09	0.1	0.01
5	4.2	0.09	0.07	0.01
4	2.1	0.07	0.04	0.01
3	2.1	0.055	0.03	0.01
2	2.1	0.01	0.02	0.01
1	0.0	0.0	0.0	0.0

Table 3: European HDD emissions legislation (g/kW-hr) for the ESC test.

Stage (Year)	*CO*	*HC*	*NOx*	*PM*
3 (2000)	2.1	0.66	5.0	0.1
4 (2005)	1.5	0.46	3.5	0.02
5 (2008)	1.5	0.46	2.0	0.02

In Brazil, Diesel engines are used in trucks and busses, however, and legislation for these has been based on the European standards. Currently, legislation equivalent to European Stage 2 is in force (ECE R49 test, 4.0 g/kW-hr CO, 1.1 g/kW-hr HC, 7.0 g/kW-hr NOx and 0.15 g/kW-hr PM). In 2006 the legislation will become equivalent to European Stage 3, and in 2009 it will be equivalent to European Stage 4 (Table 3).

Table 4: USA HDD emissions legislation (g/bhp-hr).

Year	*CO*	*HC / NMHC*[a]	*NOx*	*PM*
1998	15.5	1.3	4.0	0.1
2004[b]	15.5	0.5	2.0	0.1
2007 – 2010	15.5	0.14	0.2	0.01

a) HC applies to 1998 legislation b)

An alternative limit of NOx + NMHC = 2.5 g/bhp-hr also exisits

Legislation has been set for light vehicles (< 1700 kg) to be effective in 2007 and 2009. The test cycle is to be the FTP-75 cycle, but the legislated values are not equivalent to those in the USA legislation (Table 5). As in the rest of the world, there is a significant tightening of the NOx legislation by 2009.

Table 5: Brazilian LDD emissions legislation (g/km).

Level (Year)	*CO*	*NMHC*	*NOx*	*PM*
4 (2007)	2.0	0.16	0.6	0.05
5 (2009)	2.0	0.05	0.25	0.05

Such legislation is forcing the use of exhaust aftertreatment systems of greater complexity. To help ensure prolonged activity and durability of these systems, Diesel fuel sulfur levels are being reduced. For Stage 4 in Europe, 50 ppm sulfur fuel is required (down from 350 ppm sulfur for Stage 3), while in the US 15 ppm sulfur fuel is required in 2006 (down from 500 ppm today). In Brazil, 500 ppm sulfur fuel is the target for 2009 (although 50 ppm is proposed for metropolitan regions), and this could limit the types of aftertreatment technology applicable in this time frame.

The main aftertreatment devices for use in Diesel exhaust are discussed below.

DIESEL OXIDATION CATALYSTS (DOC)

Today, the main market for LDD vehicles is in Europe, and the majority of these vehicles currently meet Stage 3 legislation with a DOC as the only aftertreatment device. The DOC will remain a principal aftertreatment device for future vehicles, either used alone or, as discussed later, as part of more advanced emissions control systems.

The DOC principally controls HC, CO and the volatile organic fraction (VOF) of PM emissions. The legislation for these pollutants is tighter for Stage 4 than Stage 3, and there is a general trend towards lower exhaust gas temperatures and higher CO and HC emissions from LDD engines, mainly as the result of advanced engine control methods that are used to minimise NOx emissions. These factors place greater emphasis on the need for high catalyst activity at low temperatures [1, 2].

High temperature durability is important in order to withstand maximum exhaust temperatures and exotherm events that may occur on the catalyst surface (the latter usually caused by HC that can be adsorbed on the catalyst surface at low temperatures). High durability of the catalyst with respect to extended low temperature ageing is also required. Sulfur, heavy HC, and carbonaceous deposits can build-up on the catalyst surface at low temperatures and poison the catalytic activity. This ageing mechanism is particularly important because of the general trend towards lower exhaust gas temperatures on modern LDD aplications.

Figure 1 illustrates the progress that has been made in improving low temperature performance. The engine bench CO light-off activity of various catalysts is shown after extended low temperature ageing (< 320°C). A typical Stage 3 DOC demonstrates 50% CO conversion at 180°C (the T50 value) on this test. By contrast, a typical DOC suitable for Stage 4 applications has a T50 of 164°C, clearly a significant improvement. The latest developments in DOC technology demonstrate an even lower T50 value of 154°C – a 26°C improvement in light-off activity compared to a current Stage 3 DOC technology.

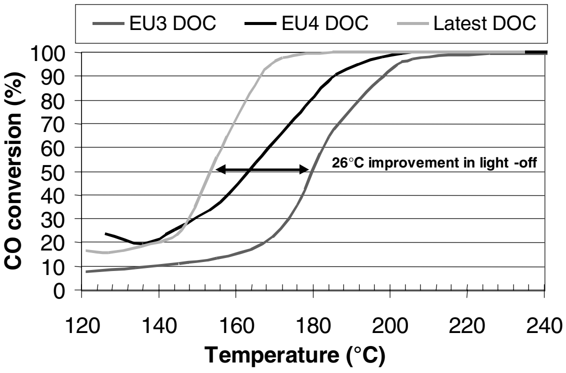

Figure 1: Engine bench CO light-off of various DOC technologies after extended low temperature ageing.

The improvement in vehicle emissions between a Stage 3 and Stage 4 DOC after extended low temperature ageing is shown in Figure 2. The improved low temperature activity of the Stage 4 DOC results in a faster light-off on the European test cycle. The improved activity enables lower emissions to be achieved with almost half of the platinum content than that used in the Stage 3 catalyst (50 g/ft^3 on the Stage 4 DOC and 90 g/ft^3 on the Stage 3 DOC). Thus the improved activity and durability of the Stage 4 DOC demonstrated on the engine bench translates to an emissions improvement at significantly lower platinum cost on a vehicle.

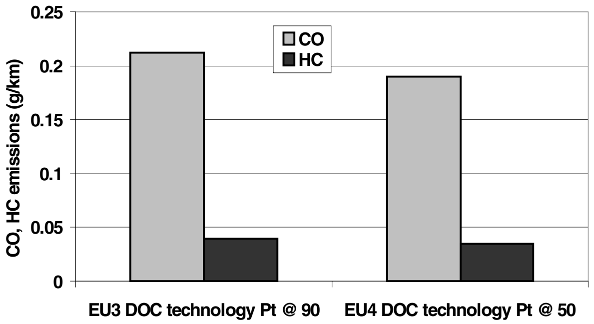

Figure 2: CO and HC emissions over the European Stage 3 test cycle (on a Stage 3 vehicle) for a Stage 3 DOC with a Pt loading of 90 g/ft^3 and a Stage 4 DOC with a Pt loading of 50 g/ft^3 after extended low temperature ageing.

DEVICES FOR CONTROL OF PM EMISSIONS

A number of methods of achieving high levels of removal of PM emissions in the exhaust of Diesel vehicles have been developed that are mainly based on a filtration technique for removal of soot from the exhaust gas.

The most common and well-known filtration devices are wall-flow filters. These filters typically consist of a honeycomb substrate and may be made from cordierite or silicon carbide (although other materials have also been employed) [3, 4, 5]. Typically, half of the cells of the honeycomb substrate are sealed at the inlet face in a checkerboard pattern, and the remaining cells are sealed at the outlet face of the substrate. When placed in the exhaust, the gas cannot pass straight through the device, but instead is forced by the seals to pass through the walls of the cells. This process results in the removal of soot (and other particles) suspended in the gas. The filtration efficiency of the wall-flow filters can be extremely high, with greater than 95% removal of particulate mass possible. This type of wall-flow filter is already fitted to a number of passenger cars in Europe [6].

Other filtration devices have also been developed. Sintered metal, ceramic foams and compacted fibres have also been demonstrated to remove PM [7, 8]. In addition, filter designs have been developed with partial flow through the filter material to give partial filtration [9].

Whatever the type of PM control device employed, the common system control issue is that soot removal by the device cannot continue indefinitely without the soot itself being removed from the system, typically by combustion. The implications of soot regeneration for LDD and HDD applications are now discussed.

CONTROL OF LDD PARTICULATE EMISSIONS

In Europe, advanced engine design and combustion control has been successfully employed in combination with low temperature light-off oxidation catalysts to reduce soot and heavy HC emissions from LDD vehicles. The contribution of sulfate emissions to total PM emissions has also been lowered by the reduction of the sulfur level in the fuel.

The further lowering of PM and NOx limits however has increased the need for PM filtration devices to meet European Stage 4 limits particularly for heavier vehicles, and for LDD vehicles to meet USA '07 limits. Improvements in engine technology can further reduce PM and NOx emissions, however, the general trade-off between NOx and PM engine-derived emissions necessitates the requirement for aftertreatment devices.

The effect on PM emissions of fitting a wall-flow filter device to a Stage 3 passenger car is shown in Figure 3. As expected, highly efficient removal of particulate is demonstrated.

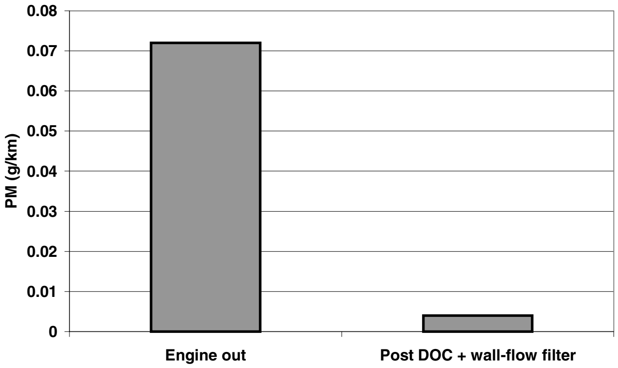

Figure 3: Effect on PM emissions over the European Stage 3 test cycle of fitting a DOC + wall-flow filter device to a Stage 3 passenger car.

In order to maintain functionality of the filter system, the filter device has to be regenerated. Combustion of soot within the filter can be achieved either by reaction with oxygen (Reaction 1), or by reaction with nitrogen dioxide (NO_2, Reaction 2). In the case of Reaction 2, a catalyst can be used to oxidise engine-out NO to NO_2 (Reaction 3), as shown in Figure 4, and the NO_2 can then react with the collected soot.

$$\mathrm{PM} + O_2 \rightarrow CO_2 \qquad (1)$$

$$\mathrm{PM} + NO_2 \rightarrow CO_2 + NO \qquad (2)$$

$$NO + O_2 \rightarrow NO_2 \qquad (3)$$

Figure 5 shows the temperatures at which soot combustion is achieved with either O_2 or NO_2 gas. The combustion of soot with NO_2 clearly occurs at significantly lower temperatures than with O_2.

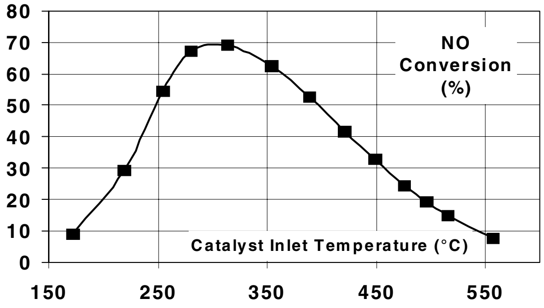

Figure 4: Temperature window for oxidation of NO to NO_2 over an oxidation catalyst.

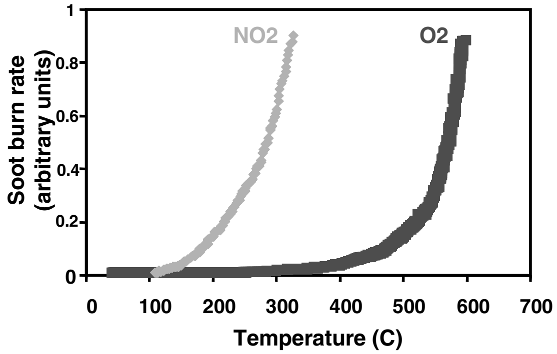

Figure 5: Combustion of Diesel soot in oxygen and nitrogen dioxide gas feeds.

In practice, the minimum temperature required to ensure a significant soot combustion rate with NO_2 is around 270°C. The soot combustion rate will also depend on the ratio of PM and NO_2 available for a given engine condition. In general, a weight ratio of around 16:1 NOx:PM is required to ensure continuous removal of soot. Under operating conditions that have sufficient temperature, combustion of the filtered soot with NO_2 can either provide continuous, or at least partial removal of soot (depending on the NOx:PM ratio), and the optimised design of the catalyst and overall system layout can maximise the efficiency of this low temperature soot combustion.

Whilst NO_2 combustion of soot can be utilised in certain driving conditions, modern LDD vehicles are characterised by low exhaust gas temperatures and low NOx concentrations emitted from the engine. The use of high levels of EGR mean that engine NOx emissions are low relative to PM emissions, and therefore the concentration of NO_2 that can be made by the oxidation catalyst is also low. Low concentrations of NO_2 result in low rates of soot burn, even if sufficient temperature is achieved in the exhaust gas. Figure 6 illustrates the effect of NOx concentration on soot combustion (monitored by the backpressure of the filter, and initial and final soot mass within the filter) on a LDD engine with and without EGR enabled at 350°C. Without EGR, there is 4.2 times higher mass flow of NOx than with EGR enabled, and a high rate of soot combustion occurred. With a high EGR rate enabled (*i.e.* as found on advanced engine applications), there is only half the amount of soot removed in the same time. Whilst complete

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