

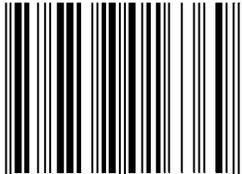
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# **Diesel Emission Control in Review**

**Timothy V. Johnson**  
Corning Incorporated

Reprinted From: **Diesel Exhaust Emission Control, 2007**  
(SP-2080)

ISBN 0-7680-1636-3



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**SAE** *International*<sup>™</sup>

2007 World Congress  
Detroit, Michigan  
April 16-19, 2007

By mandate of the Engineering Meetings Board, this paper has been approved for SAE publication upon completion of a peer review process by a minimum of three (3) industry experts under the supervision of the session organizer.

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**ISSN 0148-7191**

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**Printed in USA**

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## ABSTRACT

This summary covers the developments from 2006 in diesel regulations, engine combustion, and NO<sub>x</sub> and PM remediation.

Regulatory developments are now focused on Europe, where light-duty Euro 5 and 6 regulations have been proposed for 2009 and 2014, respectively. The regulations are less stringent than those in the US, but options exist for adopting European vehicles for the US market. Europe is just beginning to look at heavy-duty regulations for 2012 and beyond.

Engines are making very impressive progress, with clean combustion strategies in active development mainly for US light-duty application. Heavy-duty research engines are more focused on traditional approaches, and will provide numerous engine/aftertreatment options for hitting the tight US 2010 regulations.

NO<sub>x</sub> control is focusing on SCR (selective catalytic reduction) for diverse applications. Focus is on cold operation, durability, secondary emissions, and system optimization. Aged LNTs (lean NO<sub>x</sub> traps) are effective up to about 60-70% deNO<sub>x</sub> efficiency, and are being considered for light-duty and some light heavy-duty applications. There is growing interest in supplementing LNT performance with integrated SCR, which utilizes ammonia generated in the LNT during rich regenerations.

Diesel particulate filter technology is in a state of optimization and cost reduction. Very sophisticated management strategies are being utilized, which open up options for new filter materials and alternative system architectures. Secondary emissions issues are emerging and are being addressed.

## INTRODUCTION

The field of diesel emissions and control is of growing interest, world-wide. Diesel is a mainstay of the freight sector, but as its emissions decrease, diesel is growing in importance in the light-duty sector as a way of reducing greenhouse gases due to improved fuel

economy and more diversity of biofuels. As such, upwards of perhaps 1000 technical papers were published or presented in 2006 covering health effects of exhaust, fuel, engine, and emission control developments.

This paper will offer a review of a narrow aspect of this field, diesel exhaust emission control. As in the past, the review is not intended to be all-encompassing. Rather, the objective is to summarize representative studies that show the key trends in the industry. An emphasis is placed on reports from 2006. First, the regulatory issues are addressed, followed by a quick overview of engine technologies as a means of estimating the exhaust emission control requirements. Then the author will review NO<sub>x</sub>, PM (particulate matter), and hydrocarbon control developments, and close with some examples of integrated systems.

## REGULATIONS, ENGINES, AND GENERAL EMISSION CONTROL REQUIREMENTS

It is important to put emission control technologies in the perspective of regulations, which are the primary driver for advancements, and what engine technologies can reasonably deliver. The difference between the two represents the challenge to the aftertreatment technologies. Following is an attempt to summarize these needs.

### REGULATIONS

Most of the action in the new regulatory arena occurred in Europe. The US finalized their light duty, on-road, and non-road regulations several years ago. The locomotive and marine rule proposals are expected shortly. California is exploring LEV3, but no formal proposals have been put forth. Japan finalized regulations on light and heavy duty for 2009+, but has yet to harmonize with the US and Europe on non-road applications. Other countries have adopted either the European or US protocols with time lags reflective of the relative state of their transportation sectors.

Given this, the author will focus primarily on the more pertinent developments in Europe that will impact the field of diesel emissions.

### Light-Duty Diesel

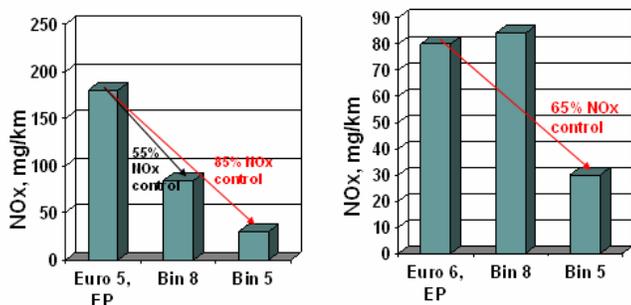
Although diesel tailpipe regulatory initiatives have already been established for the foreseeable future in Japan and the US, Europe is in the midst of finalizing their light-duty regulations for the next 10 years. On another front, the European Union and automakers came to a voluntary agreement a few years ago regarding CO<sub>2</sub> limits. California finalized similar regulations in 2005, which are currently undergoing legal review.

At the time of this writing, the European Parliament approved the Euro 5 and Euro 6 regulations, and the European Commission concurred. The final step, formal approval by the Council of Ministers, will take place very soon. They unofficially appear to accept the Parliament's version.

The regulations of significance on diesel passenger cars are as follows:

	Euro 5	Euro 6
Phase-in Dates	Sept 1, 2009 to Jan 1, 2011	Sept 1, 2014 to Sept 1, 2015
NOx	200 mg/km	80 mg/km
PM	5 mg/km	5 mg/km, plus number-based standard (tbd)

As the US market presents a large opportunity for growth of light-duty diesels, Figure 1 compares the European regulations with the US Tier 2 regulations (50,000 mile durability level) from the perspective of required additional NOx emission control measures not taking into account test cycle differences (within 10-20%). PM regulations for Bin 5 are similar. The Japan 2009 regulations are similar to Euro 6.



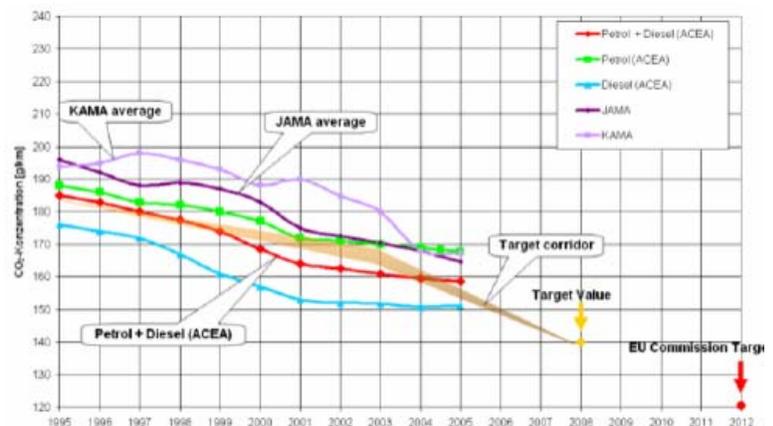
**Figure 1.** Euro 5 and Euro 6 light duty NOx regulatory proposals compared to the US. About 55-60% NOx control will be needed for a Euro 5 (2009) diesel to hit the

US Bin 8 maximum allowable emission (45 states). For Bin 5 (50 states) nominally 85-90% NOx control is needed. For Euro 6 (2014), the requirement is nominally 65% additional NOx reduction.

It is expected that the Euro 5 NOx regulations will largely be met without NOx aftertreatment (1), but significant controls will be needed to sell these vehicles in all 50 states of the US. It is more likely that Euro 6 vehicles will be developed in 2009/10 leveraging early incentive programs. Some NOx aftertreatment will be required in that timeframe on the larger vehicles. Either lean NOx traps (LNT) or selective catalytic reduction (SCR), will need to be applied to the lighter vehicles to achieve the 65% NOx control required for sales to all the states in the US. Indeed, some European manufacturers have announced Bin 5 diesels for the US in this timeframe using these two NOx control technologies.

The Parliament kept the Commission's 5 mg/km particulate matter (PM) limit and also the recommendation to implement a number-based PM requirement (number of particles per km) for Euro 6. The technical protocol for such is being developed and is close to approval, and testing and monitoring of Euro 5 vehicles for particulate number is being considered. German manufacturers have agreed to use diesel particulate filters on all cars by 2009.

Figure 2 shows how the European market is fairing regarding CO<sub>2</sub> emissions (2). In light of increasing vehicle size and capacity, and consumer desire for more power, the targets were missed for the first time in 2005, and the trend does not look favorable. As a result, the European Commission is threatening mandatory requirements. California's regulations are mandatory and similar in level, but lag the European commitment by four years.



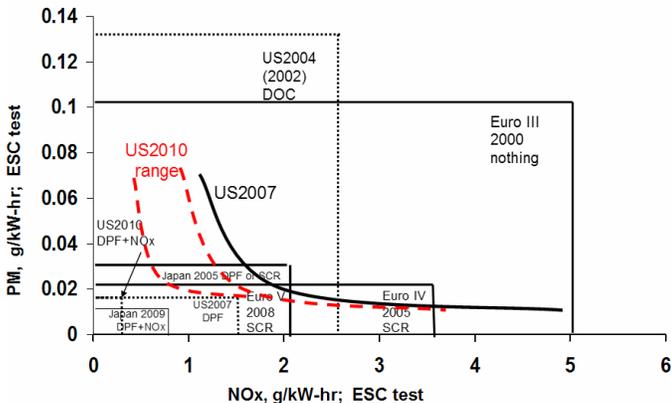
**Figure 2.** Progress towards meeting the EU voluntary CO<sub>2</sub> limits. (2)

To hit the CO<sub>2</sub> targets, Thom (2) showed that significant effort will be needed on gasoline vehicles greater than about 1000 kg and on diesel vehicles greater than about 1500 kg.

Aside from the CO<sub>2</sub> targets, there are market and political pressures on the auto companies to improve fuel economy. The combination of tighter tailpipe regulations and needed improvements in fuel economy is driving significant technology progress in the industry.

### Heavy-duty diesel

The on-road heavy-duty diesel (HDD) standards are shown in Figure 2, as are estimates of engine emissions performance. These are unchanged from the author's estimates of last year (3).



**Figure 2.** General comparison of on-road HDD standards in the US, Japan, and Europe. Estimated engine-out emissions for 2007 and 2010 (range) are shown. Steady-state cycle (3).

Japan and the US have finalized their regulations for the next five to ten years, but Europe is just beginning the process. In that regard, the European Commission asked key stakeholders to comment on six regulatory scenarios for Euro VI in the 2012-14 timeframe, ranging from no or minor tightening from Euro V to US 2010-type regulations at nominally 0.20 g/kW-hr NO<sub>x</sub> and 0.010 g/kW-hr PM. The European Commission adopted the new World Harmonized Transient Cycle (WHTC) as well as the steady state counterpart. The WHTC is cooler than the European Transient Cycle, with common engines not achieving 200°C until after 500 seconds starting with a cold engine (4). Faster light-off strategies for NO<sub>x</sub> control could become more important. Also under serious consideration are a number-based particulate standard and a heavier in-use compliance measure. The Commission is targeting having a formal proposal for the Parliament to consider by Summer 2007.

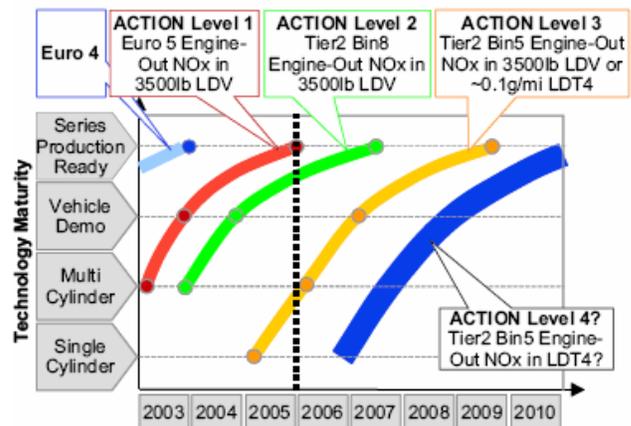
## ENGINE TECHNOLOGIES AND RESULTANT EMISSION CONTROL REQUIREMENTS

### Light-Duty

Regulatory, market, and fuel economy requirements are making great demands on the diesel engine. Further,

advanced gasoline concepts and hybrid electric vehicles are exerting competitive technology pressures. Diesel engine developers are responding by using advanced fuel injection technologies, EGR (exhaust gas recirculation) control, advanced and two-stage turbocharging, variable valve actuation, closed loop combustion control, and advanced model-based control. Advanced diesel engines (5) are now approaching 70 kW/liter specific power and 24 bar Brake Mean Effective Pressure (BMEP).

Some of these approaches show promise for allowing diesel engines to achieve Euro 6 engine-out emissions levels, and maybe even US Tier 2 Bin 5 levels. Figure 3 shows a light-duty diesel technology roadmap proposed by Cooper, et al. (6).



**Figure 3.** Light-duty diesel engine technology roadmap proposed by Cooper, et al. (6).

Each “ACTION” level increases the amount of advanced combustion utilization with high levels of EGR and other cool flame combustion strategies. The investigators project that a series–production ready 1600 kg car (3500 pounds) potentially could achieve the Tier 2 Bin 5 levels of emissions without NO<sub>x</sub> aftertreatment. It should be noted that, although this might be accomplished in principle with some engine/chassis combinations, off-cycle NO<sub>x</sub> emissions in the high-load regimes would be high and in practice would necessitate some sort of NO<sub>x</sub> aftertreatment. Further, these are very aggressive estimates given the difficulties in controlling advanced combustion under transient conditions and with acceptable engine noise under all driving conditions. Perhaps the greatest challenge for these engines is variability of key engine components and drift with age, and how this plays into the need tight combustion control (7).

In summary, Euro 5 regulations will require diesel particulate filters (DPFs) but no NO<sub>x</sub> aftertreatment. To meet Euro 6 early tax incentives in 2008 and beyond, minimal if any NO<sub>x</sub> aftertreatment will be needed on the lighter vehicles, and intermediate levels might be needed on the heavier classes. Adapting these for the US market would require nominally 65% NO<sub>x</sub> control for the

smaller vehicles and perhaps upwards of 80% total NOx control for the larger vehicles. Advanced combustion strategies, in which engine-out NOx levels over large parts of the certification cycle are very low, would require some NOx aftertreatment in the higher load regimes.

### Heavy-duty engine status

Heavy-duty diesel engine advancements are primarily aimed at improved fuel economy, reliability, cost, and durability. As such, advancements tend to be conservative and incremental. The US 2004 regulations were generally addressed using advanced EGR and turbocharging concepts. US 2007 and Japan 2005 technologies added diesel particulate filters, while Euro IV (2005) and now Euro V (2008) regulations are largely addressed using more conventional engine technologies and SCR.

Moving on to Japan 2009 and US 2010, we will also see incremental advancements from the earlier regulatory technology requirements. However, as with light-duty engines, we could see some advanced combustion strategies emerge to handle low-load emissions issues. Because most of the fuel in heavy-duty applications is spent under higher load regimes, engine researchers are focusing more on traditional diesel combustion hardware and strategies, and they are making significant progress.

Figure 4 shows a summary of high-load emissions results on research engines (8, 9, 10, 11, 12) relative to the US 2010 Not-to-Exceed (NTE) in-use emissions limits. US NTE is the most difficult standard to achieve under high load conditions in many applications. The graph shows the realm of possibilities for HD engines using cutting edge hardware and control under laboratory conditions. These results are proposed to represent the best of what technology might deliver in the next five years. With 75-80% NOx control from SCR systems under high load conditions, allowable engine-out NOx emissions of 1.6 to 2.0 g/kW-hr (without engineering margin) put PM emissions at about 0.025 to 0.050 g/kW-hr, placing PM NTE requirements well within the range of filters.

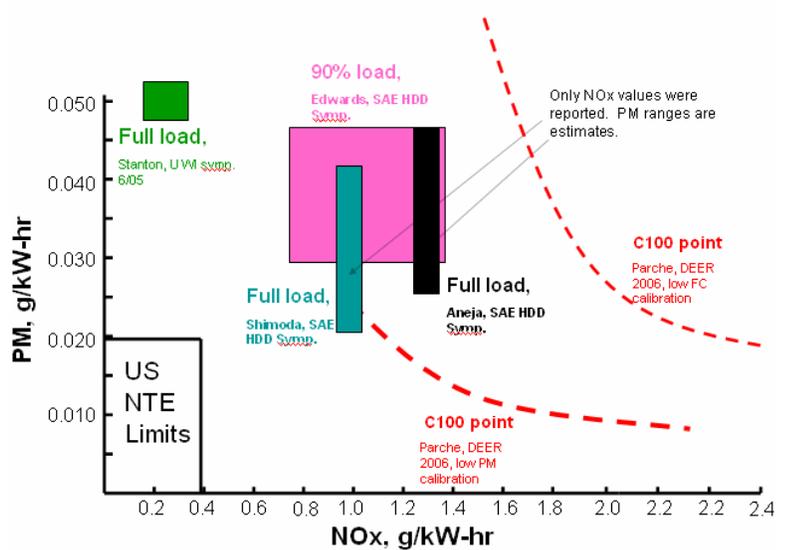


Figure 4. High load steady-state test results on HD research engines relative to the challenging US Not-to-Exceed in-use regulatory requirement.

US 2007 engines need to meet NOx NTE levels of about 2.3 g/kW-hr. Without advancements, these engines need about 85% NOx control to hit the US 2010 NTE requirements. With 90% efficient filters, PM NTE is not an issue. A typical 2007 high load point would be well off the graph in Figure 4. It is reasonable to believe that actual 2010 engines may incorporate nominal 20% incremental improvements that are based upon the 2007 technology.

### NOx CONTROL

Given the tight NOx emission regulations in the US and Japan, and the fuel economy impacts NOx aftertreatment can have, NOx control technologies will play a key role going into the future. Following is an assessment of the state-of-the-art on selective catalytic reduction (SCR) and lean NOx traps (LNT). Very little was in the literature in 2006 regarding lean NOx catalysts.

### SELECTIVE CATALYTIC REDUCTION

Although NOx control was not required to meet the Euro IV or Japan 2005 HDD regulations (beginning October 2005), SCR was selected by several truck manufacturers because the high NOx efficiencies in the tailpipe allow the engine to be run at higher NOx levels for better efficiency and lower PM, thus delivering competitive fuel economy and eliminating the need for a DPF. In the US, the EPA released a proposed guidance document that laid out its requirements for SCR: no operation without urea, and conveniently located urea filling stations (13). One approach the EPA proposed to the first requirement might be to use interlocks that are engaged if the urea:fuel ratio is out of balance right after fueling.

Jackson, et al, (14) evaluated the US urea market and concluded that with vehicle manufacturer commitment to SCR in 2007, there is reasonable time to implement an appropriate urea infrastructure using bottles for LD applications for Model Year 2009, and using pumps for HD by 2010. Figure 5 shows the authors' urea cost sensitivity estimate relative to the monthly urea throughput for the filling station. For light-duty, the assumed urea consumption rate is 2% relative to the fuel, and with a 28 liter tank the urea fill interval is about 18,000 km. As such, urea could be replenished at the lube oil shop, and bottles could be used if necessary in the interim. For HD applications, the urea consumption rate was assumed to be 1%, and in this case a 75 liter tank will last 21,000 to 27,000 km. Like in the LD case, this is greater than the lube oil change interval for most medium duty and vocational applications, but line haul vehicles would need one urea fill on the road. However, this author believes 1% urea consumption is underestimated for line haul applications. For example, given an SCR system operating at 85% efficiency at highway load points, about 2.2 g/kW-hr NOx is reduced to hit the NTE requirement of 0.39 g/kW-hr NOx. The urea consumption at this level of NOx reduction is 3 to 4%.

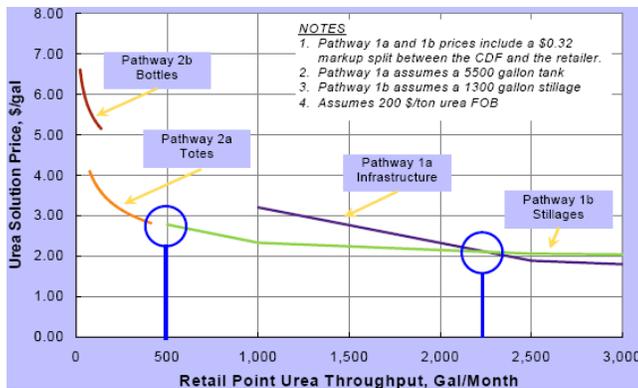


Figure 5. Urea price declines as the monthly throughput of the filling station increases. \$2.00/gal is about \$0.53/liter. (14)

Ammonia can be provided for SCR from solid urea or from newly reported storage compounds. Mueller (15) reported on advancing solid urea usage from the conceptual to the detailed engineering stage, looking at urea decomposition rates as a function of heating rate and pellet size under a variety of conditions. A 13 liter container of pellets (9.5 kg) will last 40,000 km when used to take a Euro 3 car to Euro 4 (0.25 g/km NOx reduction). Similarly, a 25 liter container will last 25,000 km on a truck with a 2 g/kW-hr drop in NOx. Johannessen (16) propose the use of  $MgCl_2$  as a storage medium for ammonia (forms  $Mg(NH_3)_6Cl_2$ ). The storage density is 3X that of liquid urea and only 10% less than liquid ammonia. It weighs 60% less per unit of ammonia than liquid urea. In use the medium would be heated to nominally 180°C to release the ammonia gas (100 W delivers 0.5 g/min  $NH_3$ ). In light-duty applications a 60 liter tank could last the 150,000 miles in taking a Bin 8

diesel to Bin 5. One concept has the rechargeable canisters being replaced at a service interval, and then recharging them at a central facility.

Op de Beeck and Joubert (17) provide a good review of SCR integration into LD and HD vehicle systems. Of particular interest is the stability of urea under high temperature conditions. They report that for a pick-up truck operating under high load in hot ambient conditions (Arizona) with a urea delivery rate of 10 to 30 kg/hr, the urea in the tank heated due to the return line but never exceeded about 60°C. Urea decomposition rates at this temperature are about 17% over 30 days, or insignificant over the operation of the vehicle.

Urea decomposition limits the effectiveness of SCR at exhaust temperatures of less than about 200°C. Kawatari, et al. (18) uses a heated slip stream in the exhaust to hydrolyze urea for use under low load conditions. One result at 1000 rpm is shown in Figure 6, in which the heated slip stream allowed the SCR to operate at >90% deNOx efficiency at 150°C, compared to 70% efficiency using normal exhaust urea injection. At 1260 rpm, the differences were even more profound.

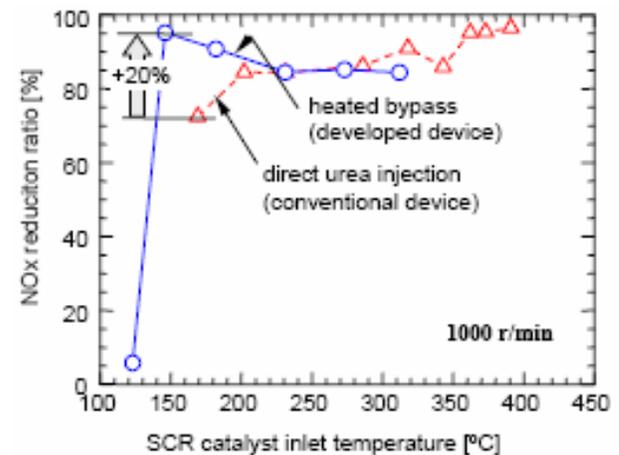


Figure 6. Decomposing urea at low exhaust temperatures using external heating provides a step improvement in SCR performance at T<200°C at 1000 rpm. (18)

SCR catalyst development is providing new alternatives to vanadia or zeolite formulations. Hamada, et al., (19) report on a vanadia-free titania-based multifunction catalyst primarily developed as an ammonia slip catalyst. In that function, the wash-coated catalyst converted 250 ppm ammonia primarily to nitrogen at T>200°C and a space velocity of 100,000/hr. They compare this to conventional catalysts that don't become active until 250°C, and primarily form  $N_2O$ . The catalyst family also performs respectably as an SCR catalyst, but sacrifices performance relative to conventional alternatives at T<250°C.

Finally, Lambert, et al., (20) discuss some of the issues in integrating an SCR system with filters in a light-duty application. To address Bag 1 cold start NO<sub>x</sub> (60% of the total in their configuration), they put the SCR catalyst ahead of the filter. Tailpipe emissions are close to Bin 5 for lightly-aged systems, but they miss the 120,000 mile requirement due to durability issues. In their system the filter has no passive regeneration capability (no NO<sub>2</sub>), so during the more-frequent active regenerations, the upfront DOC and SCR need to heat to soot burning temperatures. This requires very durable DOC and SCR catalyst formulations. Figure 7 shows that new zeolite formulations can tolerate occasional exposure to 800-850°C and still maintain acceptable performance.

## LEAN NO<sub>x</sub> TRAPS

Lean NO<sub>x</sub> traps offer an attractive NO<sub>x</sub> solution for light-duty applications and those HD applications in which an extended urea infrastructure might be problematic. In US HD applications the challenge for LNT is acceptable high temperature efficiency to meet the NTE requirements (50-70% control at 500-520C), and do it over the useful life of the vehicle (185,000 miles for medium HDD and 435,000 miles for heavy HDD). On the light-duty side, efficiencies need to be high enough to hit Tier 2 Bin 5 (70% using traditional diesel combustion; 30-50% in the 50 to 70% load range using mixed mode combustion) over the useful life of the vehicle (120,000 miles).

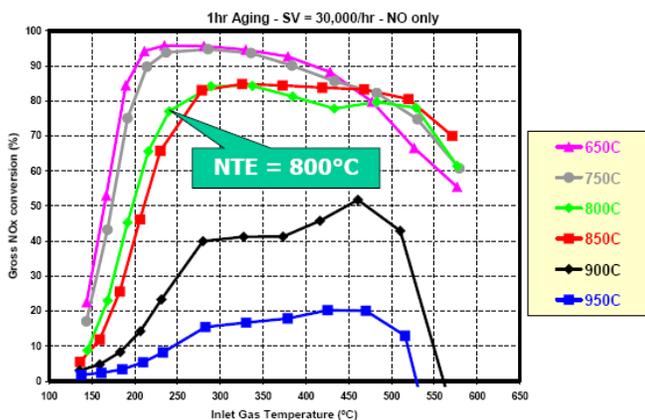


Figure 7. New zeolite SCR catalysts show impressive durability when occasionally exposed to temperatures of 800-850°C. (NTE refers to not-to-exceed temperature for design purposes.) reference 20.

Dual leg LNT systems are of interest because only a part of the exhaust stream is used during rich regeneration, saving fuel. Tsumagari, et al., (21) refined the switching strategy when going from the lean to the rich leg to drop the total size of LNT to 10.4 liters on a 7.7 liter engine (SVR=1.4), while minimizing the effective fuel penalty to 1.4% and maintaining a 80% efficiency at full load and speed.

Achieving high efficiency with a fresh or lightly aged LNT is quite common. Dorenkamp (22) shows that indeed, an LNT that starts out at 90% efficiency deteriorates to 60% efficiency after 30,000 km, but then stabilizes. Rohr, et al. (23) substantiate this by subjecting LNTs to aggressive desulfation cycles. After severe aging, two LNT formulations achieved nominally 60-65% deNO<sub>x</sub> over the US LD test. Other investigators more closely evaluated LNT deactivation by investigating migration of Pt and/or Ba in the catalyst, and Pt sintering (24).

## LEAN NO<sub>x</sub> TRAP PLUS SCR SYSTEMS

The most interesting development of 2006 regarding NO<sub>x</sub> treatment is the expansion of work done on adding an SCR after the LNT to improve efficiency or decrease cost. The principle is that ammonia formed during the period rich NO<sub>x</sub> regeneration (a few seconds every minute) is stored in an SCR catalyst and utilized to reduce NO<sub>x</sub>, from rich slip or during lean operation. A system similar to the one reported by Lambert last year (25) is now in series production (26). This is the most basic system, with an SCR catalyst following the LNT.

Hu, et al., (27) refine this system further by adding a fuel reformer in front of the LNT to produce hydrogen during the rich periods. The hydrogen promotes the formation ammonia in the LNT. In this configuration the SCR adds up to 20% incremental NO<sub>x</sub> efficiency to the LNT operating at 60-70% efficiency. Further, the hydrogen which is also produced during the rich desulfation helps remove sulfur, thus helping to extend the minimum desulfation frequency by 30%.

Hemingway (28) add another dimension to the architecture by using an off-line plasma-based reformer and an LNT bypass. In this configuration, exhaust is bypassed to the SCR while reformat is used in a throttled LNT leg during the rich regeneration. The system offers the potential advantage of generating more hydrogen, decreasing the desulfation temperature to reducing aging effects, and making hydrogen available to enhance DPF regeneration and perhaps low temperature LNT performance (29).

Finally, Satoh, et al. (30) consolidated the SCR function onto the NO<sub>x</sub> adsorber using a double layer. The concept is shown in Figure 8. The NO<sub>x</sub> adsorber is ceria-based with a platinum catalyst to promote the formation of ammonia during the rich cycles. The released ammonia is captured by the top zeolite SCR catalyst, and is made available during the lean cycle for NO<sub>x</sub> reduction. The system is fundamentally different from the others in a number of ways. First, the ceria is not a nitrate-forming NO<sub>x</sub> trap like the traditional LNTs. The NO<sub>x</sub> is chemisorbed. As such, it has excellent low temperature efficiency, but it falls off at 350°C. Further, as the sulfate is also loosely bound, desulfation can occur at temperatures as low as 500°C, compared to 650-750°C for traditional formulations. Finally, as the

SCR deNOx function is effectively upstream of the NOx adsorber during lean operations, all of the ammonia is utilized for deNOx potentially with simpler logistic control.

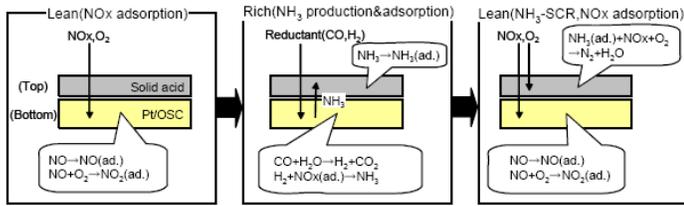


Figure 8. SCR catalyst is added on top of a ceria-based NOx adsorber to take advantage of ammonia generated from the adsorber during rich regeneration. (30)

### LNT AND SCR COST COMPARISONS

Johnson (31) did a first pass cost analysis of LNT and SCR systems for a light-duty application. The results are shown in Figure 9. In the analyses, the system size, washcoating and substrate costs, exhaust sensors, and canning cost are assumed to be the same. The incremental differences are due to catalyst cost (mainly precious metal) and on-board urea system costs. For traditional diesel combustion engines larger than 2 to 2.5 liters, SCR is more economical. However, as advanced combustion mixed-mode engine technologies are introduced, LNT precious metal loadings can come down significantly because most of the precious metal is used to address NOx at  $T < 350^{\circ}\text{C}$  (32). In this case, the engines in which SCR is more economically attractive are increased to displacements larger than about 5 liters.

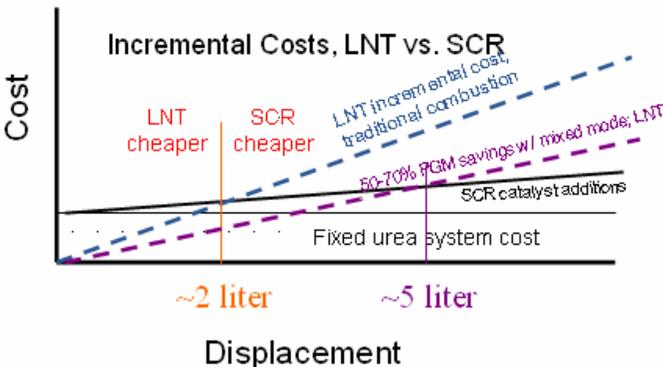


Figure 9. Incremental costs of LNT vs. SCR as a function of engine displacement, assuming canning, substrate, and washcoating costs are the same. (31)

### NOx ON-BOARD DIAGNOSTICS

An update was provided on NOx sensors (33). After aging, the accuracy is at about  $\pm 15\%$  today, going to  $\pm 10\%$  by 2010. Ammonia adds to the sensor output signal. Kim and Nieuwstadt (34) used mathematical arguments to show that for an Tier 2 Bin 5 SCR system operating at 70 to 83% efficiency and a NOx sensor with  $\pm 12\%$  accuracy and no ammonia slip the minimum OBD

threshold of detection is 2.5 to 3.5X the standard. This compares to the California minimum detection threshold of 1.75X the standard by 2013. The main levers to reduce the threshold are further improvements in accuracy and offset error (ammonia slip is a contributor).

### PM CONTROL

Diesel particulate filters have been commercially applied on passenger cars in Europe for more than 7 years, but are beginning to go commercial for HD applications, with Japan 2005 and US2007 regulations coming into force. Despite that the field is generally in an optimization and cost reduction stage, developments and understanding is still advancing rapidly. Although the LD and HD applications have their differences, the similarities dominate. As such, this section consolidates LD and HD developments.

### REGENERATION

Plewnia (35), presented a comprehensive overview of a filter regeneration system that utilizes a fuel born catalyst. Components of the strategy are a soot loading estimator that utilizes a soot map and driver usage profile, system heat up using increased electrical load, if necessary, and initiation of regeneration upon accelerator pedal pullback to minimize feel of increased torque with late or post injections. They replaced one large post injection with two small ones to minimize oil dilution by fuel and to give better combustion stability. The cycle average filter penalty for DPF management is 2%.

Although SiC has been the main filter material for light-duty applications, the technology is advancing to enable alternative materials, such as cordierite. Pidria, et al. (36) did a laboratory investigation on soot burning rates as a function of oxygen content and flow rate using cordierite filters. At a soot loading of 9.5 g/liter, they report that at the higher flow rates, oxygen content of the gas had little impact on the peak burn temperatures in the filter. Similarly, at lower flow rates, there was not enough oxygen flux to create a large exotherm. Only at intermediate flow rates, 100 to 150 kg/hr, did oxygen have an impact. They used this information to develop a cordierite DPF system for a light duty platform, and presented that, even at soot loadings as high as 19 g/liter no damage to the filter was observed using the strategy during worst-case regenerations.

Similar to Craig, et al., (37), Maramatsu, et al. (38) investigated the impact of exhaust temperature and soot loading on peak DPF temperatures in cordierite filters. However, they added another degree of sophistication to such models by looking at soot morphology and oxidation rates as a function of the operating conditions of the engine. Depending on the reactivity of the soot, the threshold between a safe and a damaging

regeneration with cordierite filters, as a function of soot loading and exhaust inlet temperature, was determined. Figure 10 shows their result.

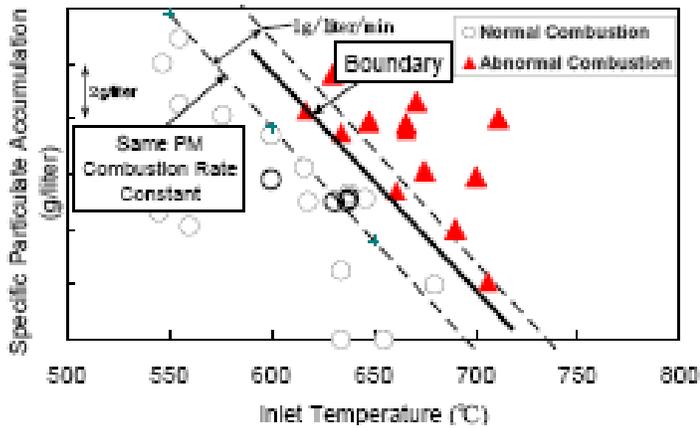


Figure 10. The threshold between normal and abnormal regenerations for cordierite filters depends on soot loading, DPF inlet temperature, and soot reactivity (dashed lines). Reference 38.

Fuel penalties due to DPF regeneration are being minimized. Dorenkamp (22) shows that when filter components are put in the close coupled position, post injection time can be reduced from 17 minutes for a catalyzed filter in an underbody position to less than 10 minutes when moved close to the turbocharger. Others (39) show that cordierite heats to soot burning temperatures in half the time of SiC. Most of the fuel savings is due to much lower thermal conductivity for the cordierite.

Andersson, et al., (40) show that particulate ultrafine emissions can depend on how soon after a regeneration the measurement is taken. Their results are shown in Figure 11. The figure shows that ultrafine emissions taken immediately after a regeneration at 4X those immediately before due to loss of the efficiency-enhancing soot filter cake. They also show that during a filter regeneration aerosol nanoparticle emissions temporarily increase, quite markedly.

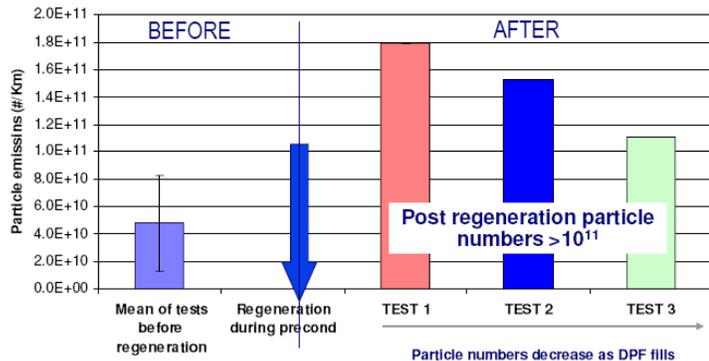


Figure 11. Ultrafine emissions increase 4X immediately after a regeneration. (40)

Finally, there is much interest in the impact of biodiesel blends on DPF performance. Williams, et al. (41) investigated the impact B20 and B100 (20% and 100% soybean-source blends) fuels have on PM loadings and soot compositions and DPF regeneration temperatures. Soot loadings dropped nominally 25% with the two biodiesel blends versus neat fuel, the organic carbon to elemental carbon ratio (OC/EC) increased 4X, and the soot burning temperatures dropped 100C° due to changes in soot morphology.

### FILTER MATERIALS AND CATALYSTS

Aluminum titanate DPFs went into production in 2006. Kercher, et al., (42) describe the development process and DPF auxiliary hardware. Of note is that it is the first application of a close-coupled catalyzed filter without a DOC. The aluminum titanate also showed impressive durability. A sectioned filter shows no cracks after surviving 55 uncontrolled and 90 controlled regenerations.

SiC filters are seeing further improvement (43). A more resilient paste between segments relieves stresses in the skin region that are especially troublesome for longer filters. The outer skin crack temperature limit is increased from 900 to 1150°C as a result.

Miyazaki, et al., (44) provide a “macro-micro” analytical model that utilizes stress analyses at cell wall intersections, resulting in much more efficient and reliable mechanical analyses of cellular ceramic materials.

Punke, et al., (45) describe a method of incorporating the DOC function onto the DPF – zone coating of the catalyst. In this method, a higher catalyst loading is applied to the front of the filter relative to the back, thus segregating the filter into various functions. The investigators show similar hydrocarbon and CO oxidation performance relative to with a DOC, and similar or better regeneration depending on degree of zoning.

Ogyu, et al. (46) provide some interesting results on moving wall flow filters to more of a depth filter design by opening up the porosity. They show that the soot oxidation rate at 20% regeneration and 530°C nearly doubles if the average pore size increases from 11 to 35 µm. It increases another 3X if the pores are enlarged to 50 µm. The authors show that improved catalyst/soot contact offered by a more even distribution of the soot is the reason for the improvement. However, filtration efficiency is sacrificed in that the 50µm pored filter had only 60% filtration efficiency, compared to typically 90%+ for finer pores. The authors thought the efficiency could be improved with changes in geometry.

Finally, mat material is used to hold the DPF in the can. This is more difficult than presumed due to an order of magnitude difference in the expansion of the metal can

relative to some ceramic materials as temperature increases. Further, converse to other applications, the mat material needs to sustain adequate canning pressures at much higher temperatures, and provide excellent thermal insulation properties. Fernandes, et al., (47) describe three types of recently advanced DPF mats with different behavior for holding pressure versus temperature and shrinkage versus gap bulk density.

## ASH MANAGEMENT

Dacosta et al., (48) report on the effect that phosphorous ash from the lube oil has on catalyzed filter performance. The doped fuel that was fed into an exhaust injector with a phosphorous containing compound, and simulated 600,000 and 1,200,000 miles (960,000 and 2,000,000 km) of phosphorous accumulation (8 and 16 g/liter). Surprisingly, and unexplained, the unloaded filtration efficiency of bare and catalyzed cordierite filters decreased with phosphorous exposure. Catalyst activity was also shown to decrease, with the soot burning temperature shifting higher by about 50 to 100C° with the intermediate aging, and complete catalyst deactivation after the severe aging.

Aravelli, et al., (49) shed some light onto the ash mass balance puzzle. Like others, they show that the amount of ash collected on filters might be <50% of the ash expected based on lube oil consumption. Filters are known to have very high trapping efficiency of ultrafine particles, typically 99%+ in the size range of the fundamental ash particle. At least some of the “missing ash” might collect in the oil sump. The investigators show that seven metals associated with ash increase in concentration in the oil sump after 500 hours of operation. Regarding the impact of ash on DPF filtration dynamics, they show an initial pressure drop for filters with soot loading as the ash begins building up a filter cake on the cell wall, Figure 11. The authors explain that without this ash layer, soot can penetrate into the walls, causing a marked increase in back pressure. With a small ash layer, this penetration is prevented.

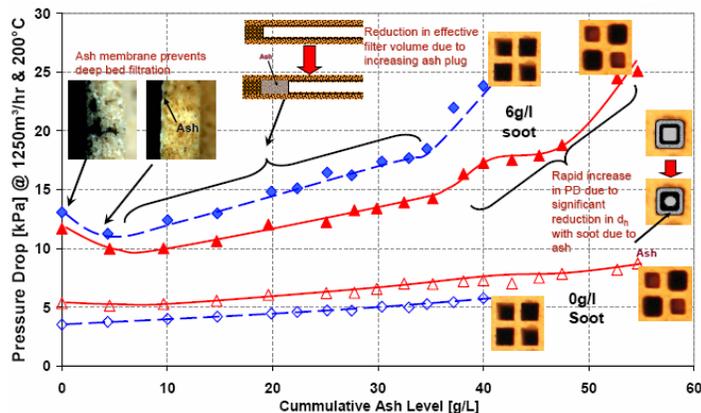


Figure 11. An initial ash layer prevents soot from penetrating the wall, resulting in lower back pressure upon soot loading than without ash. The triangles refer to an asymmetric cell geometry that provides more ash storage capacity. (49)

Finally, in a very comprehensive paper on cleaning ash from filters, Nuzskowski, et al., (50) use back pressure models and ash measurements to assess cleaning time using water and air on different filter types. They show in Figure 12 that most of the ash is removed after about 20 minutes of cleaning with air. Back pressure measurements tend to underestimate ash removal, and water was more effective in removing stubborn ash, but may impact mat materials.

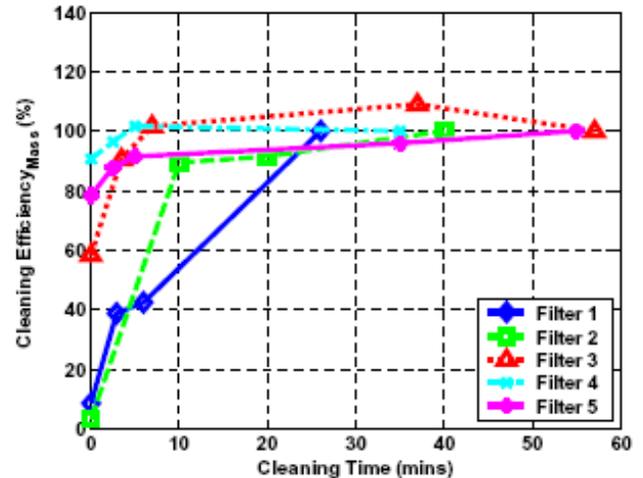


Figure 12. After about 20 minutes of cleaning with shop air (827 kPa pressure), most of the ash is removed from five different filters that were investigated. (50)

## SECONDARY EMISSION ISSUES

Many filter systems use catalyst to form NO<sub>2</sub> to help oxidize the soot under many operating conditions, and/or to burn hydrocarbons to heat the filter to soot oxidation temperatures. The catalyst can create sulfate aerosol nanoparticles and excess NO<sub>2</sub>.

Kittelson, et al. (51) provide good insight into current understanding of ultrafines. Diesel engine ultrafine particulates can be broadly classified into solid soot particles in the 50-300 nm size range, and smaller aerosol nanoparticles (5-50nm) primarily formed by the condensation of sulfuric acid. The paper shows that DPFs take down soot emissions to nearly immeasurable levels, but do little to remove aerosol nanoparticles. Under some operating conditions DPF systems can actually create aerosol nanoparticles. Sulfur dioxide formed from the combustion of fuel and lube oil is oxidized by exhaust catalysts to form sulfur trioxide under higher load conditions, which then combines with water to form sulfuric acid nanoparticles. Use of ultra-low sulfur fuel and low-sulfur lube oil are shown to have some positive impact, but ultrafines can still increase upwards of 100X relative to engine-out emissions under highway cruise conditions. Figure 13 shows that with a sulfur trap in the exhaust system, the aerosol nanoparticles are virtually eliminated.

NO<sub>2</sub> mortality was recently estimated at 0.3% per 10 µg/m<sup>3</sup> increase in the atmosphere (52). Although this is a fraction of the mortality generally attributed to PM, and all NO from exhaust converts to NO<sub>2</sub> in the atmosphere in less than an hour under most conditions, NO<sub>2</sub> from the exhaust can result in high personal exposure rates and can negate much of the benefit from filters and DOCs. In response, the California Air Resources Board recently placed limits on the amount of NO<sub>2</sub> that can be emitted by approved retrofit filter systems – the tailpipe NO<sub>2</sub> cannot be increased relative to the engine out amount by more than 30% beginning in 2007, and no more than 20% is allowed in 2009. Goersmann, et al., (53) present a solution wherein a catalyst is added after a catalyzed filter system that converts NO<sub>2</sub> back to NO using injected fuel (HC:NO<sub>2</sub><1).

## CONCLUSIONS

The following conclusions are derived from the coverage of the current literature on emissions control. The regulatory framework for on-road diesel engines through 2013 is described, as well as emerging engine technologies. This helps define the future aftertreatment requirements. In general, for LDD using incremental advances in traditional diesel combustion, although DPF will be needed, nominally no NOx aftertreatment will be needed to meet most applications for Euro V and likely Japan 2009. US Bin 5 will need additional 70% NOx control from Euro 6 engines, and DPFs. As mixed mode combustion develops, Bin 5 passenger cars will likely require minimal NOx aftertreatment perhaps as early as 2009, followed by the same status for heavier LD vehicles in 2011. For HDD the Japan 2009 regulations show good chances of being hit with advanced combustion, at least as indicated by today's research engines, but NOx control will likely be extended from Japan 2005 to offer better fuel economy. For US 2010, research engines are showing greatly reduced PM at engine-out NOx levels that can be addressed with NOx aftertreatment.

For NOx control, LNTs will meet the LDD requirements of nominally 70% reduction, and SCR leads the HD field. The middle sized applications could go either way. New SCR catalysts are emerging with increased durability and better ammonia slip conversions. For LNTs, durability is established at about 60-70% efficiency for well-aged systems. Combination LNT+SCR systems are being reported that convert NOx on the LNT to ammonia during the rich regeneration, which in turn is stored on the SCR catalyst for additional NOx removal during the lean treatment.

Filters are continuing the movement towards cost reduction and performance improvement. DPF regeneration strategies are enabling cordierite filters in light-duty applications. For the first time, ash cleaning methods are quantified. Filter secondary emissions are being addressed.

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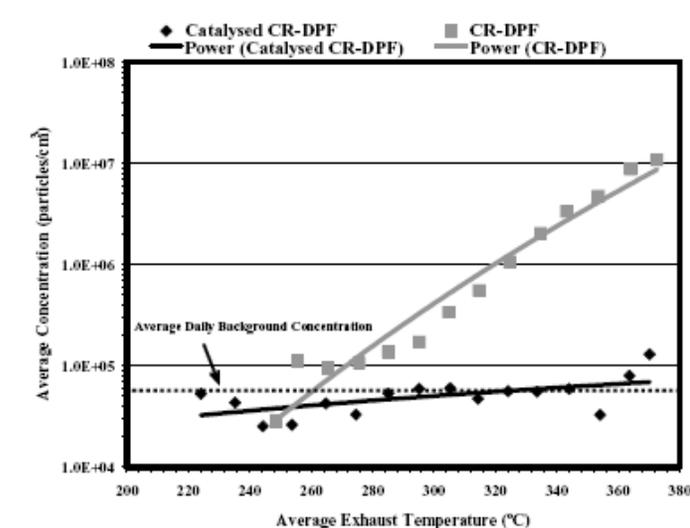


Figure 13. The average number of ultrafine particles increases with exhaust temperature primarily due to the formation of sulfuric acid aerosol nanoparticles (boxes). If the sulfate can be trapped, the ultrafine particle concentration in the exhaust is less than in ambient air. (51)

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