Diesel Emission Control Technology

SYSTEM CONTAINING PLATINUM CATALYST AND FILTER UNIT REMOVES PARTICULATE FROM DIESEL EXHAUST

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Recent concerns over the health effects of particulate emissions from vehicles have focused on diesel engines. While European legislation to limit their emissions is now in place it is expected that future legislation will be more demanding. Using a platinum catalyst it has been possible to demonstrate in various trials the practical application of a novel system for the removal of both the soot and hydrocarbon components from diesel powered vehicle exhaust. The background to the development of this successful technology is described here.

Diesel engines find widespread application as power sources in both mobile and stationary applications. Their innate high efficiency and economy have resulted recently in unprecedented growth in their share of the passenger car market in Western Europe. The durability of the diesel engine has also led to its dominance as a source of motive power for the transport industry.

However, the ubiquity of large diesel-engine vehicles in city environments has persuaded regulatory authorities of the need to control the emitted exhaust pollutants. European legislation limiting the quantities of carbon monoxide, hydrocarbon, oxides of nitrogen and particulate matter were introduced in 1993 and will be strengthened in 1996. However, in spite of the tightening standards, a large fleet of long lived and rather polluting diesel vehicles exists in most cities around the world.

Diesel Exhaust

Diesel exhaust differs from that of petrol engine exhaust in two major characteristics. Firstly, diesel exhaust contains a far higher amount of particulate material, and secondly the exhaust is far "leaner", that is, it is far more oxidising than the typical exhaust from petrol engines (1).

The health effects of diesel particulate have been a cause of concern for many years, because of both the chemical composition and the particle size spectrum (2). The two major components of particulate are soot and heavy hydrocarbons – the soluble organic fraction, SOF – which condenses on it during its collection. The SOF is known to contain carcinogenic polyaromatic hydrocarbons (3), however, the beneficial effect that oxidation catalysts have on the toxicity of diesel exhaust by removing SOF is well documented (4, 5).

A body of evidence implicating the soot fraction of diesel particulate as damaging to human health has recently begun to emerge. The nature of the effect appears to relate not to the chemical nature of the soot, which is predominantly carbon, but to its particle size (6). A significant quantity of airborne urban particulate is known to derive from the exhaust of diesel engines (7). In studies in the United States, very close correlations have been noted between particulate air pollution and mortality rates (8) and the California Air Resources Board has stated that there is likely to be no threshold limit below which particulate does not represent a finite health risk (9).

The diesel emissions standards for heavy duty vehicles, extant and proposed for the European Union, are shown in Table I. A bus, for example, with a 200 kW engine, which meets the 1993 standards for particulate will, if it conforms to the average emission levels measured in the steady-state test by which its engine is certified for production, emit around 80 grams

Table I

Current Legislation (from 1 July 1992) According to Directive 91/542/EEC

Application dates	Mass of CO, g/kW h	Mass of HC, g/kW h	Mass of NOx, g/kW h	Mass of TPM, g/kW h
1 July 1992 new vehicles 1 Oct. 1993 all vehicles	4.5 (4.9)	1.1 (1.23)	8.0 (9.0)	0.36* (0.4*)
1 Oct. 1995 new vehicles 1 Oct. 1996 all vehicles	4.0 (4.0)	1.1 (1.1)	7.0 (7.0)	0.15* (0.15*)
Test Procedures:	1 July 1992 - ECE R49 1 October 1995 - ECE R49			
Figures in ( ) refer to conformity of production				

* In the case of engines of 85 kW or less, a coefficient of 1.7 is applied to the limit for particulate emissions
CO is carbon monoxide, HC is polyaromatic hydrocarbons, NOx is nitrogen oxides and TPM is Total Particulate Matter

of particulate per hour. Therefore, a large fleet of vehicles, which may frequently be older, or may simply not conform to current type-approval standards, will emit a significant mass of particulate into urban environments.

The awareness of the growing concern over these issues has caused Johnson Matthey to reassess the methods by which particulate can be removed from diesel exhaust (10). While the effect of an oxidation catalyst on the polyaromatic hydrocarbons in diesel exhaust is clearly beneficial, it has little or no effect on the quantity of soot. The net particulate mass, which includes SOF, is reduced by an oxidation catalyst, because the hydrocarbons, which co-condense with soot particles, contribute to it.

Filtration is a technique which has been widely studied for the removal of soot from diesel exhaust (11). As soot is collected on a filter placed in the exhaust stream of a diesel engine the pressure drop across the filter increases. The increased engine power which is required to drive the exhaust gases through the filter, causes the exhaust temperature and also the fuel consumption to rise. Soot combusts at 550–600°C, but it is not sufficient to rely on an increased pressure drop to generate the temperatures required in the exhaust gas to initiate the combustion, and damage to the engine under these conditions is a significant risk.

The regeneration of soot filters through soot combustion has been the subject of much work over 20 or more years, and techniques such as in-line fuel burners, catalytic fuel burners and electric heaters have all been examined. Catalyst technology has also been investigated in an attempt to lower the temperature at which the oxidation of soot commences (12). For many years it had been assumed that the mechanism by which such systems began to regenerate the filter traps involved the adsorption of particulate on the catalyst in close proximity to an oxygen activation site.

In the course of experimental work at Johnson Matthey to define the conditions necessary for the catalytic regeneration of traps we uncovered a novel mechanism (13, 14). Carbon, in the form of soot, was being oxidised, not by "activated" oxygen, but by nitrogen dioxide. The diesel combustion process is characterised by higher pressures in the cylinders than occurs in spark ignited engines. The rate of formation of nitrogen oxides (NOx) in the combustion process is at least partly a function of the oxygen available, and so the higher pressure and leaner mixture of diesel engines tend to produce

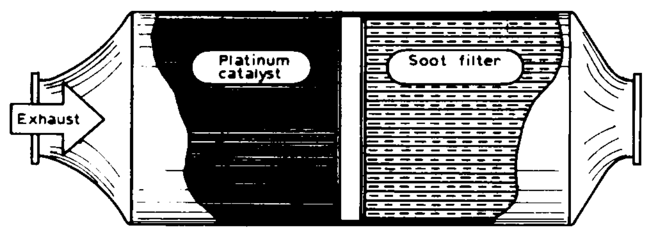


Fig. 1 The platinum catalyst, loaded at 50 g/ft^3, is mounted on a substrate of cell density 400 cell/in^2. The cordierite soot filter has alternate blocked channels, and is known as a "wall-flow" filter

more NOx. The majority of NOx emerges from the engine as nitric oxide, and it is the conversion to nitrogen dioxide, over a catalyst using the excess oxygen present in the exhaust gas, and its subsequent reaction with carbon, which is responsible for the observed depression in the temperature at which a catalysed exhaust filter can be regenerated.

It was also concluded that the nitrogen dioxide required for the reaction could be supplied upstream of a reactor containing a non-catalysed filter trap. The generation of nitrogen dioxide and the oxidation of carbon were observed to be independent processes. Catalyst formulations were investigated and platinum upon alumina was found to be the most active. Since the processes of soot trapping and soot destruction are continuous at temperatures above 275°C, we have chosen to refer to a system based on this technology as a "Continuously Regenerating Trap" or CRT.

It was foreseen at this time that application of this discovery would be problematic because of the high level of sulphur which was then present in diesel fuel. Highly active oxidation catalysts convert sulphur dioxide, formed by the oxidation of fuel-derived sulphur components during combustion, into sulphur trioxide. Sulphur trioxide adsorbs water and condenses on the filter which is used to measure particulate mass. Thus, if a high sulphur fuel is used, a significant increase in particulate mass will be recorded in standard regulatory tests where a catalytically regenerated filter is used to remove soot and SOF.

We have been prompted to re-examine the applicability of this technique as a consequence of a number of changes that have occurred in recent years. The principal changes are the availability of low sulphur diesel fuel and the widespread use of turbocharged diesel engines.

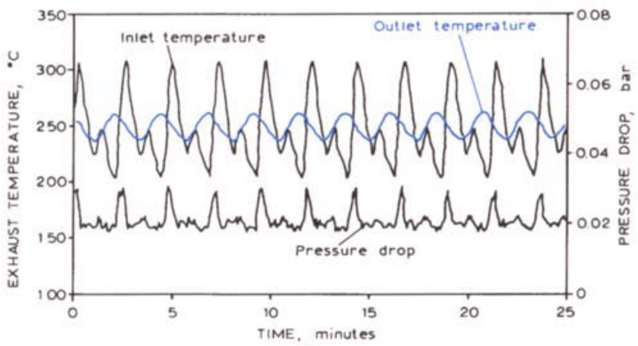
Construction and Performance of the System

The systems that have been tested used both ceramic catalyst substrate and ceramic filters. Ceramic filters consist of an extruded ceramic (cordierite) monolith with a low cell density, typically of 100 channels/in^2, in which alternate channels are blocked at one end. As the exhaust gas enters a channel, it is forced through the channel walls into an adjacent channel to exit

Table II
Conversion Efficiencies in Recognised Cycles

Test cycle	Sulphur content of fuel, per cent	Conversion, per cent		
		TPM	**HC**	**CO**
ECE R49 (13 mode)	0.005	80	96	99
U.S. HDT, catalyst I	0.05	87	98	99
U.S. HDT, catalyst II	0.05	92	94	99
Braunschweig (bus)	0.005	92	96	98

Fig. 2 Semi transient ageing for the Continuously Regenerating Trap system, showing the variations with time of the exhaust temperatures into and out of the filter system and the pressure drop across the filter. Back pressure bahaviour remained consistent over 1000 hours



the filter. For this reason these devices are often referred to as "wall-flow" filters. The separate catalyst substrate, shown in Figure 1, had a cell density of 400 cells/in^2 and was coated with a layer of washcoat having a platinum loading equivalent to 50 g/ft^3. Extruded ceramic monoliths were chosen for these tests because of their well characterised filtration capabilities and because there is substantial experience on their application to diesel exhaust purification (15, 16). Catalyst and filter parts were separately wrapped with a mat of insulating material and welded into steel skins. These were then located in a cylindrical steel shell with appropriate inlet and exit gas distribution configurations, designed and constructed by Eminox Ltd. of Gainsborough. The degree of sound attenuation of this type of device adequately reproduces that of a conventional silencer. Thus, when mounting such a system on a vehicle, the filter system is able to be fitted as a replacement unit with great simplicity, provided that the existing unit is not located too far from the exhaust manifold of the engine.

In order to assess the performance of the system it was first mounted on a laboratory engine bench, and tests were conducted using both ECE R49 and U.S. Heavy Duty Transient (U.S. HDT) cycles on a 6 litre, 6 cylinder engine. The pollutant reductions measured in these two regulatory cycles are shown in Table II. In the case of the Heavy Duty Transient test two catalyst variants were used, the first (catalyst I) was of a slightly higher activity and showed a superior hydrocarbon conversion. The slightly lower net particulate conversion is almost certainly due to a small conversion of sulphur dioxide to sulphur trioxide in the hottest mode of the cycle.

The durability of the system was first examined in laboratory tests using an engine of the same type. A "semi transient" ageing cycle was developed to mimic the long continuous operation of an engine under rather cool conditions. The cycle is shown in Figure 2. The pressure

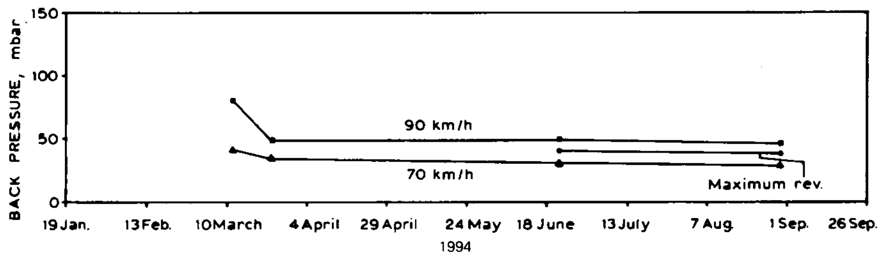


Fig. 3 Back pressure shown over a period of almost 6 months for a mail truck fitted with a CRT

Table III

Particulate Conversions
(Mail truck CRT after 1000 hours ageing and 58,000 km)

Temperature, °C	Maximum, per cent	Minimum, per cent	Average, per cent
250	99	98	98
380	96	94	95
450	73	33	51

drop across the filter was measured over an ageing period of 1000 hours during which no increase was observed.

Practical Trials

The results of these tests were extremely encouraging and several systems have been fitted to vehicles in normal use. The stainless steel filter systems were placed in the same location on the vehicles as the original equipment silencers. This was achieved without significant alteration to the vehicle, as the systems are dimensionally similar to the conventional silencers. In one trial, a unit which had been aged for 1000 hours in the laboratory was fitted to a mail delivery truck which had an engine capacity of 7 litres (245 hp). Pressure drop measurements taken on the vehicle in service over a period of almost six months, during which it travelled a total distance of 58,000 km, are shown in Figure 3. The data shows a remarkably consistent level of pressure drop with no increase observed during the trial. At the end of the period shown the unit was removed from the vehicle and again tested on the laboratory engine. The results are shown in Table III.

In another example, a system was fitted to a city bus having a 10 litre engine (285 hp). The results of this whole-vehicle test are shown in Figure 4. After running for several weeks the bus was tested on a chassis dynamometer using the so-called Braunschweig driving cycle. This cycle has been designed to reproduce, using a complete vehicle, the type of driving experi-

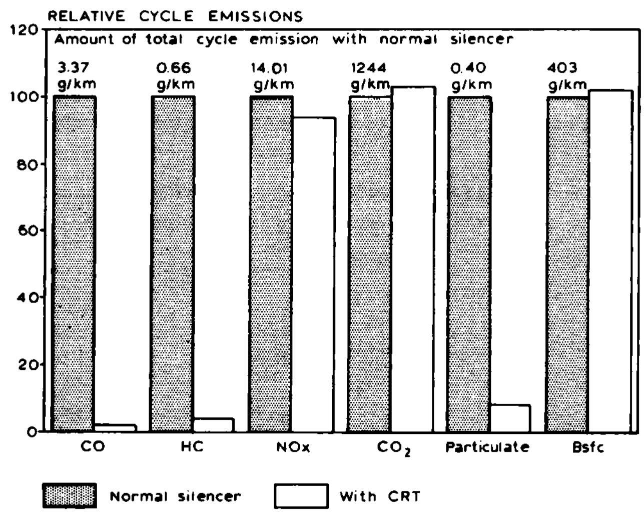


Fig. 4 Tests performed using the Braunschweig cycle on a Volvo bus fitted with a CRT system. Relative cycle emissions are shown for a normal silencer (100 per cent) and with a CRT installed. Bsfc is the brake specific fuel consumption

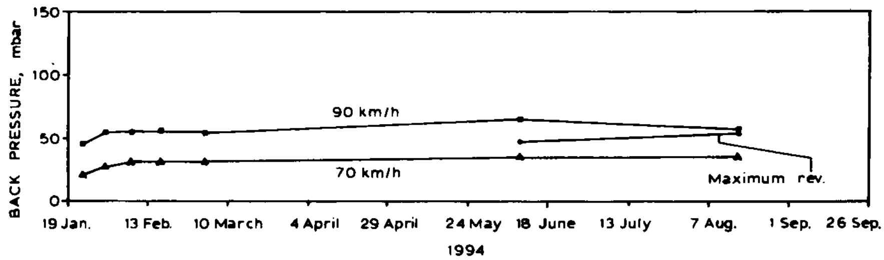


Fig. 5 Back pressures displayed by a refuse collection truck fitted with CRT, over a period of 7 months

enced by a bus in a typical urban application. Normal regulatory tests involve removing the engine from the vehicle and so do not reflect its true on-road dynamic emissions behaviour. Conversions of 98 per cent carbon monoxide, 96 per cent hydrocarbons, 6 per cent NOx and 92 per cent particulate were observed in the cycle. A small increase in carbon dioxide emissions was also noted. This derives from the oxidation of carbon monoxide, hydrocarbons and soot as well as from a 1 to 2 per cent increase in fuel consumption.

To-date some 23 systems have been fitted to heavy duty vehicles in Sweden including buses, delivery trucks and refuse collection trucks. The observed back-pressure behaviour for a refuse truck which covered only 10,000 km over a period of seven months' heavy operation is shown in Figure 5. This is a particularly difficult duty cycle for a filter system since the engine spends much of its time operating with rather a cool exhaust, see Figure 6 which shows a typical temperature trace. All these systems have demonstrated a similar lack of pressure drop build-up as those described above.

Discussion

The original work on filter regeneration temperatures suggested that a temperature of below 300°C was achievable, and this work confirms that regeneration is occurring at or below 275°C. This is important because it must be possible to regenerate the filter at temperatures routinely reached in the exhaust of a vehicle operating under normal conditions.

From the work undertaken so far it is clear that this technology is applicable to situations where three basic criteria have to be met, namely:

- There should be a reasonable balance between the levels of NOx and particulate emitted by the engine
- The duty cycle of the vehicle should regularly give rise to an exhaust temperature above 275°C
- The engine should be run on low sulphur fuel.

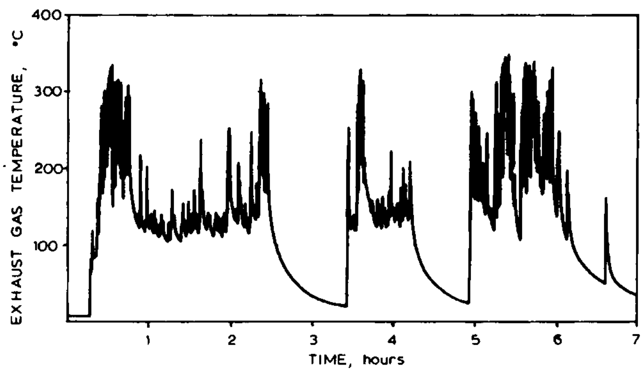


Fig. 6 Temperature at the CRT inlet on a refuse collection truck over its normal operating cycle

In our tests of normally operating vehicles we have found that a fuel sulphur level of below 100 ppm will give rise to a very satisfactory performance. Our laboratory data suggest that we will be able to extend this level of confidence to diesel fuel containing 500 ppm in the near future. This is a key level, since diesel fuel will have a legislated maximum sulphur content of 500 ppm in the U.S.A. and the E.C. by the year 1996.

However, the technology cannot be applied as a panacea to old and dirty engines. In particular it has been noted that old fashioned heavy-duty engines which have pre-chamber combustion systems and are not turbocharged frequently give rise to smoky exhausts. The balance of NOx and particulate in such exhausts does not make this a suitable system for them.

The experiments we have performed to-date indicate that filter performance has remained remarkably invariant during the trials. This contrasts to much of the previous experience with filters, and especially experience with wall-flow ceramic filters. With this new technology, the low temperature of filter regeneration, and the fact that regeneration is a continuous process, leads to a significant reduction of thermal and physical stress on the filter units. These considerations would seem to indicate that the filters will have a long lifetime. However, this system does not excuse poor engine maintenance, and in the event of the failure of, for example, a turbocharger, the balance of particulate and NOx may be significantly altered so as to prevent effective regeneration. In order to take account of such servicing needs it is envisaged that the system will be of modular construction. The filter unit can then be removed from the vehicle and exchanged without needing to demount the whole assembly.

Conclusions

Diesel engines of recent manufacture, and engines which have been designed to meet the current and future emission limits, will continue to emit substantial quantities of particulate into the urban environment. The advent of readily available low sulphur diesel fuel in 1996 brings with it the possibility of using a novel form of exhaust filter regeneration technology which has shown great promise in early trials. To-date more than 20 vehicles have been fitted with systems that have been shown to remove a substantial proportion of the hydrocarbons and particulates in the exhaust gas which are the cause of growing concern amongst health experts.

Further work is being undertaken to characterise and develop the performance of the system. The apparent simplicity of the technology, totally without any moving parts or complex control systems, is an added feature which will appeal to operators and owners of vehicles alike.

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