

# Flow-Through Catalysts for Diesel Engine Emissions Control

## PLATINUM COATED MONOLITHS REDUCE PARTICULATES

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The treatment of vehicle emissions with an exhaust catalyst in order to reduce the level of three major air pollutants, namely carbon monoxide, unburnt hydrocarbons and nitrogen oxides, is becoming a world-wide requirement for gasoline fuelled engines (1, 2). First standards were introduced in the U.S.A. and Japan during the early 1970s (3). Similar standards will be enforced in Europe beginning in 1992/93 (4, 5). Diesel engine exhaust poses an additional challenge for emission control because, as compared to exhaust from gasoline engines, it also contains particulate matter. Early attempts at particulate control utilised catalytic trap oxidisers to filter the exhaust and oxidise the particulates (6–8). Catalytic trap oxidisers have the disadvantage of requiring an active regeneration mechanism to remove particulate build-up. Recent advances in diesel

engine technology have greatly reduced the formation of particulates, with the result that air quality standards may now be met by the use of catalysed flow-through monoliths (9–11). These catalysts have the advantage of being passive systems which do not require regeneration.

Catalysts for diesel engines must function differently to those for gasoline engines because of differences in the chemical composition of the exhaust gas. Modern spark-ignition gasoline powered automobiles, with emission control devices, operate near stoichiometry (at an air:fuel ratio of ~14.7:1) and under closed-loop electronic control. The catalyst typically operates in the temperature range of 300 to 900°C and functions by oxidising carbon monoxide and unburnt hydrocarbons to carbon dioxide and water, while oxides of nitrogen are

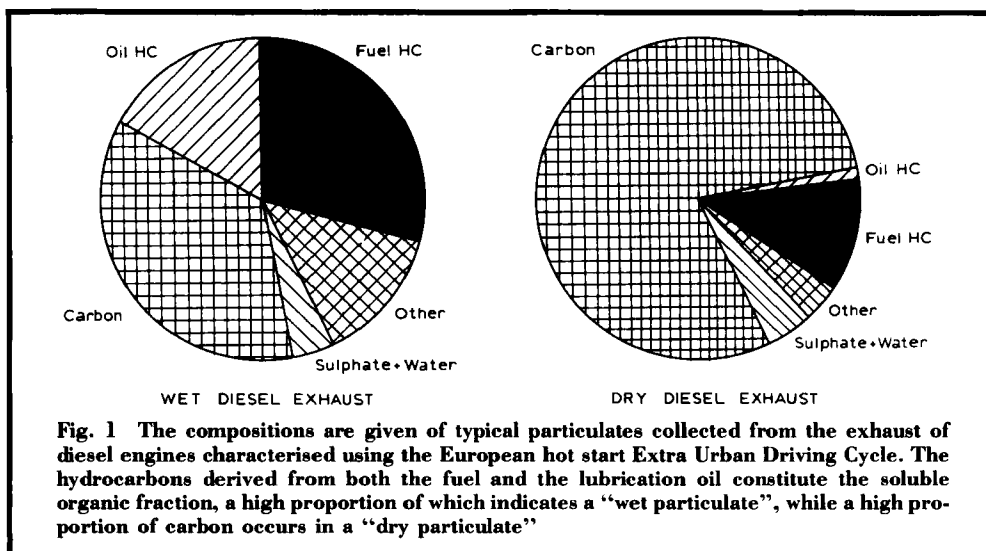


Table I  
**Current and Proposed World-wide Diesel Emission Laws**

Market	Test	Class	HC	CO	NO <sub>x</sub>	HC + NO <sub>x</sub>	Particulate
U.S. 1987	FTP g/mile	LD	0.41	3.4	1.0		0.20
California 1989	FTP g/mile	LD	0.39*	7.0	0.4		0.08
U.S. 1991	HDT g/hph	HD	1.3	15.5	5.0		0.25
U.S. 1994	HDT g/hph	HD	1.3	15.5	5.0		0.10
Japan 1990	10 Mode g/km	LD HD	0.62 0.62	2.70 2.70	0.70 0.84		None None
Japan 1994	10 Mode g/km	LD HD	0.62 0.62	2.70 2.70	0.50 0.60		0.2 0.2
EC 1992	ECE + EUDC g/km	Auto		2.72		0.97	0.14
EC proposed Stage 1 1992/93	EC steady state test g/kWh	HD	1.1	4.5	8.0		0.36
Stage 2 1995/96	EC steady state test g/kWh	HD	1.1	4.0	7.0		0.15

FTP Federal Test Procedure  
HDT Heavy Duty Truck  
EUDC Extra Urban Driving Cycle

LD light duty  
HD heavy duty

\* Non methane hydrocarbons

reduced to nitrogen gas (12–16). The standard practice for gasoline exhaust treatment is to utilise a noble metal catalyst supported on a flow-through ceramic or metallic monolith, typically having 300 to 400 axial channels per square inch of frontal area. The monolith walls are coated with a thermally durable, high surface area oxide on which are supported the active catalyst components, generally platinum, palladium and rhodium.

Combustion of diesel fuel occurs by high pressure ignition, rather than by spark ignition, and at air:fuel ratios greater than 20:1. The

exhaust temperatures are typically cooler, 150 to 450°C, and are always oxidising. The diesel engine generates intrinsically low emission levels of gas phase hydrocarbons and carbon monoxide, and when fitted with a conventional oxidation catalyst there is little trouble meeting regulated standards for these pollutants. The use of typical three-way catalysts to control nitrogen oxide emissions is impractical due to the oxidising nature of the exhaust. Therefore, nitrogen oxide emissions must be controlled by engine design and calibration, often at the expense of increased particulate emissions. As a

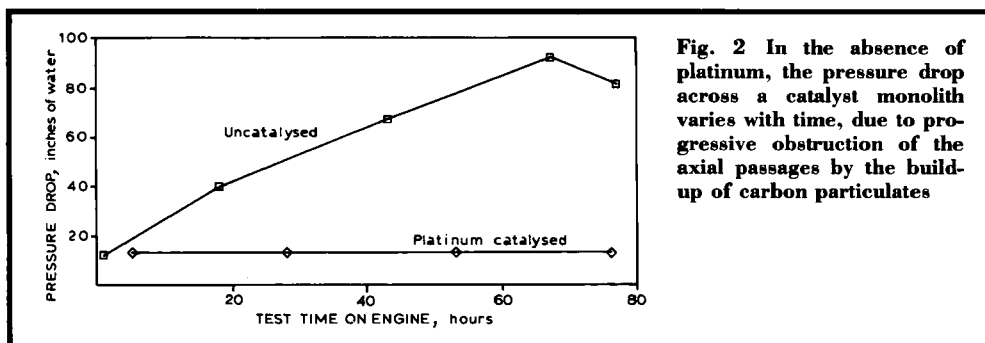


Fig. 2 In the absence of platinum, the pressure drop across a catalyst monolith varies with time, due to progressive obstruction of the axial passages by the build-up of carbon particulates

result, the major challenge to diesel exhaust emission control by catalytic means remains one of particulate removal. Additionally, in Europe, where there is a combined hydrocarbon + nitrogen oxide standard, removal of low temperature gas phase hydrocarbons is beneficial to meeting the overall design requirements.

There are a variety of diesel engine designs and these may be classified according to the method of fuel and air injection, as well as by the end-use application. Engines with indirect injection of fuel are typically utilised for passenger cars and light-duty trucks, while direct injection engines have inherently better fuel economy and are utilised in heavy duty vehicles. Many manufacturers are developing high speed direct injection engines for use in light-duty applications. Air is added to the combustion chamber by natural aspiration or under pressure by turbocharging, and turbocharging is often accompanied by intercooling. World-wide emissions standards for diesel fuelled engines will finally require the use of catalytic converters in the 1992-94 time frame, see Table I.

### Diesel Particulate Catalysis Particulate Composition

Diesel particulate standards are measured via the weight increase of a fibre filter placed in the diesel exhaust. The material collected consists of graphitic "hard" carbon or "soot", a soluble organic fraction (SOF), water, sulphuric acid and an inorganic ash residue. Typical particulate compositions are given in Figure 1. The

soluble organic fraction consists of hydrocarbons derived from both fuel and lubricating oil which condense as the exhaust cools, or adsorb during collection. The sulphuric acid/water fraction arises from oxidation of sulphur dioxide to sulphur trioxide and condensation with water vapour.

### Importance of Sulphur in Diesel Particulate Control

Sulphur is present to some extent in all diesel fuel and, as a result of the combustion process, is emitted in the exhaust as sulphur dioxide. A small fraction, typically about 2 per cent, is further oxidised to sulphur trioxide which condenses with water in the exhaust as sulphuric acid, and is then absorbed on carbonaceous soot particles, thus contributing to the total measured mass of particulate emissions. The use of a catalyst can increase the fraction of fuel sulphur converted to sulphate, and even a modest increase in this fraction will result in the "manufacture" of significant particulate. For example for a 0.05 weight per cent sulphur fuel, 100 per cent conversion of the sulphur in the fuel to sulphuric acid would by itself result in a particulate emission five times higher than the 1994 U.S. heavy duty truck standard.

### Particulate Control Strategy

A "flow-through" monolithic reactor, as opposed to a particulate trap, achieves particulate reduction by catalytic oxidation of the soluble organic fraction. However, this will result in minimal conversion of the hard carbon, and therefore, the catalyst must be able to keep

itself free from particulate fouling. During low temperature operation particulate increase via sulphuric acid formation is not significant, but under these low temperature conditions it is necessary for the catalyst to remove the soluble organic fraction and the gas phase hydrocarbons. During high temperature operation the oxidation of hydrocarbon is facile, but the increase of particulates due to sulphate formation must be minimised or eliminated.

### Catalytic Carbon Oxidation

It has been reported previously that the removal of carbon requires reaction with nitrogen dioxide, which is formed by the oxidation of nitrogen monoxide over a platinum catalyst (17). Palladium and rhodium are much less effective for the oxidation of nitrogen monoxide at low temperatures, and their inclusion with platinum in a catalyst formulation results in de-activation of the platinum. In the absence of platinum an increase in back pressure in a flow-through system has been observed as a function of time, see Figure 2. This emphasises the requirement for platinum in the catalyst formulation in order to prevent fouling by carbon particulate.

### Catalytic Sulphur Oxidation

Similar to carbon oxidation, it has been demonstrated that platinum is the most effective catalyst for sulphur dioxide oxidation, that palladium and rhodium are less active, and that the alloying of palladium or rhodium with platinum results in a compromise activity.

Sulphur dioxide adsorbs strongly on platinum at room temperature and inhibits carbon monoxide, nitrogen monoxide and alkene oxidation. Sulphur dioxide oxidation is kinetically limited at low temperature and thermodynamically limited at high temperature, but near 500 to 600°C can reach 80 to 90 per cent conversion. Factors which can limit sulphur dioxide oxidation activity in this temperature range include oxygen concentration, space velocity (Figure 3), and intrinsic catalytic activity.

### Removal of the Soluble Organic Fraction

Hydrocarbon species in diesel exhaust consist of gaseous compounds as well as heavy, condensable hydrocarbons (soluble organic fraction) which can be solubilised from the diesel particulate. The soluble organic fraction is both fuel and oil derived, and has been characterised by gas chromatography-mass spectroscopy (18, 19). As with the oxidation of sulphur dioxide and nitrogen monoxide, platinum is generally considered the best low temperature hydrocarbon oxidation catalyst, with palladium or rhodium being both less effective and/or poisons for platinum. At high temperatures complete oxidation is favoured.

### Emission Characteristics of Diesel Engines

To demonstrate the variability in emission composition with engine type and operating conditions, test results for two diesel engines

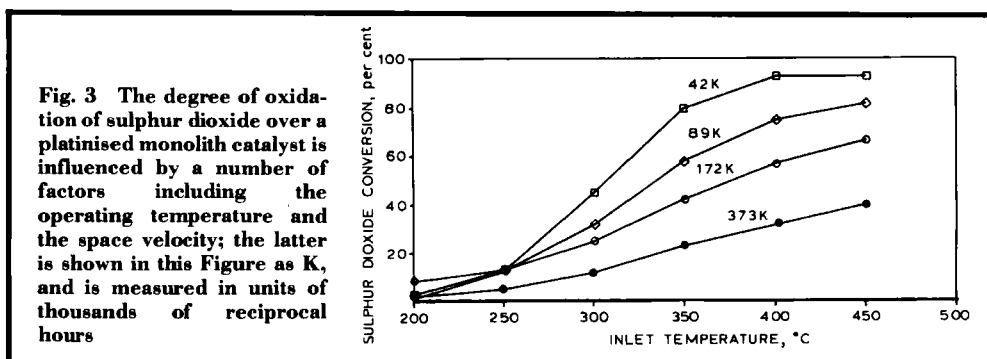


Table II Baseline Diesel Emissions*					
Test	Engine **	HC	CO	NO <sub>x</sub>	Particulate
FTP g/mile	A	0.18	0.64	0.96	0.24
	B	0.13	0.81	0.76	0.16
EUDC g/test	A	0.51	1.67	3.31	0.95
	B	0.42	2.02	2.89	0.75
Hot SS g/test	A	1.87	5.72	12.2	2.79
	B	0.86	5.54	7.95	2.27

\* (mean of triplicate testing)

SS steady-state

\*\* Engine A: 1.6 l IDI-TC indirect injection—turbocharging  
Engine B: 1.8 l IDI-NA indirect injection—natural aspiration

Table III Baseline Gaseous Hydrocarbon Emissions						
Compound	FTP (mg/mile)		EUDC (mg/test)		HOT SS (mg/test)	
	Engine					
	A	B	A	B	A	B
Methane	48.2	105	109	220	315	594
Ethylene	27.4	26.8	68.5	60.2	346	148
Acetylene	7.3	10.6	21.2	25.6	67.8	69.5
Propylene	11.5	8.4	27.8	23.6	145	65.8
1-Butene	~9	7.5	~20	12.7	~65	12.3
Isobutene	~9	6.7	~23	13.3	~145	48.7
1,3-Butadiene	5.6	9.4	14.8	14.5	79.2	18.0
Benzene	~4	7.1	~12	18.4	~29	51.2
Toluene	~6	11.7	~34	19.5	~36	33.4
Ethyl benzene	~15	15.7	~34	34.7	~135	90.0
p- and m-Xylene	~23	42.2	~115	67.6	~78	143
o-Xylene	~16	19.8	~28	23.4	~111	133
Formaldehyde	15.2	33.3	59.3	152	210	166
Acetaldehyde	8.5	30.4	55.1	119	105	155
Acrolein	3.0	8.1	11.2	26.9	53.7	34.8
Acetone	2.5	5.6	13.9	10.6	37.3	13.4
Propionaldehyde	3.0	2.9	8.3	6.2	20.5	6.9
Crotonaldehyde	0.7	2.6	2.7	5.2	16.3	10.0
Benzaldehyde	2.5	5.3	8.5	12.8	34.6	24.1

**Table IV**  
**Baseline Particulate Emissions**

	Fuel HC	Oil HC	SOF	Carbon	Sulphate + Water	Other
FTP Percentage of total particulate mass						
Engine A	7.0	22.4	29.4	40.4	2.0	28.2
Engine B	16.9	6.4	23.3	63.7	2.6	10.4
EUDC Percentage of total particulate mass						
Engine A	29.8	16.2	46.0	36.1	4.2	13.7
Engine B	11.4	<1.0	~ 11.4	79.3	4.7	3.6
Hot SS Percentage of total particulate mass						
Engine A	15.3	16.6	31.9	39.5	4.4	24.2
Engine B	7.0	<1.0	~ 7.0	80.2	4.5	7.3

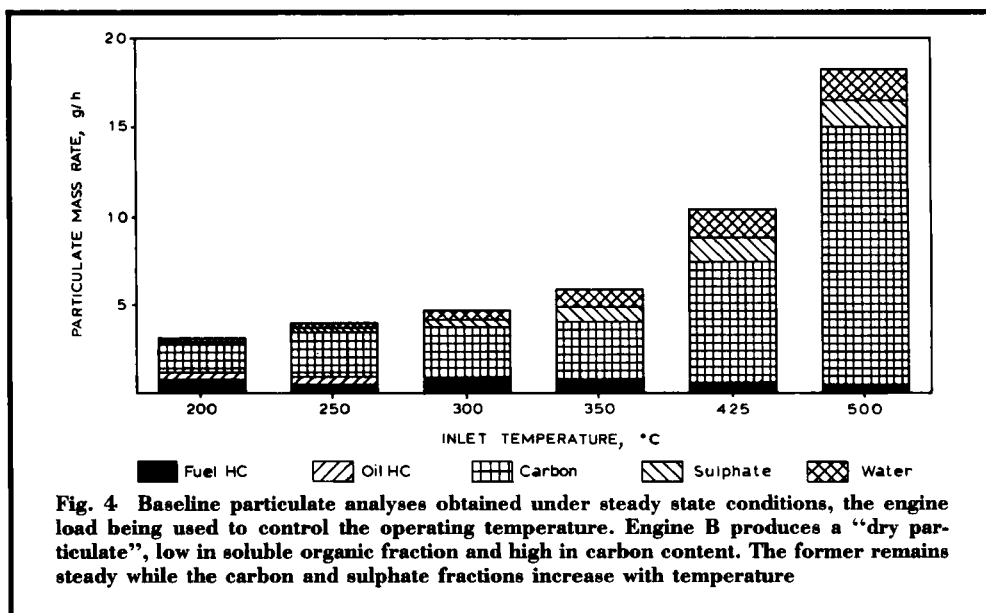
are given in Table II (20). The engines were characterised using the U.S. cold start Federal Test Procedure, the European hot start Extra Urban Driving Cycle and a hot steady-state test with inlet temperature in the range of 400 to 420°C. The emitted gaseous components and particulates measured without a catalyst fitted to the engines are given.

The gaseous hydrocarbon fraction resulting from incomplete fuel combustion was analysed in further detail and, as shown in Table III, was composed primarily of methane, and unsaturated, cyclic and oxygenated hydrocarbons. The aldehyde/ketone components are generally considered to be responsible for the offensive odour associated with diesel engine exhaust.

The composition of the particulate component of diesel emissions is dependent on the combustion process, as controlled by engine design, the lubricant and the fuel used. The sulphate content was analysed by ion chromatography, the soluble organic fraction

was extracted and subsequently characterised into fuel derived and oil derived fractions by gas chromatography, and the carbon content was quantified by thermogravimetric analysis. The remaining component has not been fully characterised, but represents the inorganic zinc, calcium, and iron compounds derived from lubricants and from engine wear. The particulate analyses, for all three vehicle test cycles, are shown in Table IV, and illustrate some specific engine characteristics which are important when designing a catalyst for particulate attenuation control.

Engine A showed a consistently higher soluble organic fraction and would be considered to produce a "wet particulate", with low carbon content and high soluble organic fraction. While Engine B could be described as forming a "dry particulate", low in soluble organic fraction and high in carbon content. The differences in emissions can be partially explained by the differences in operating temperature,



with the hotter engine resulting in a “drier” particulate. Thus Engine B represents the more difficult system to treat catalytically, and would present the greatest challenge.

### Catalyst Development

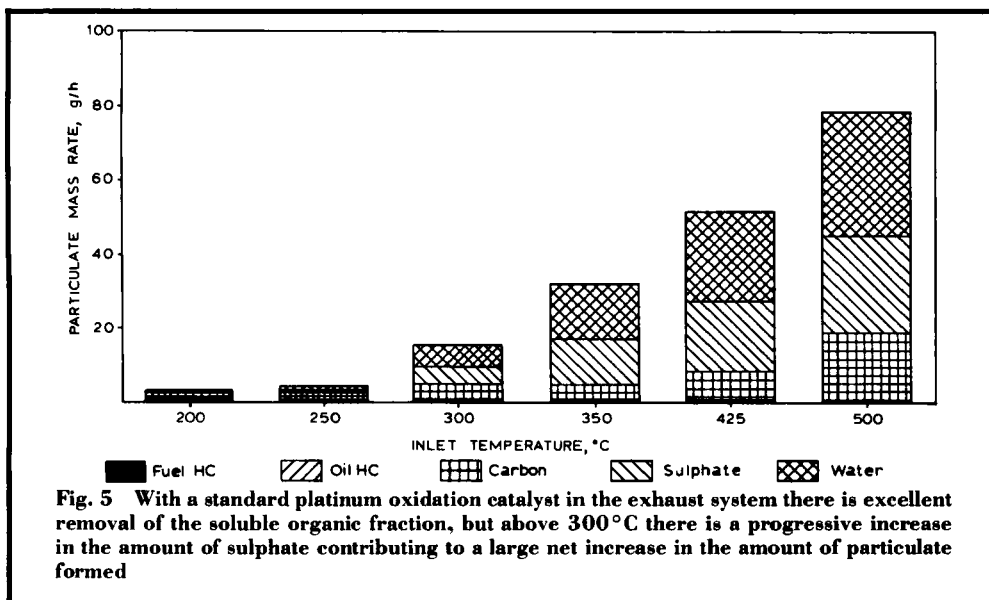
The challenge for diesel catalyst development is to reduce the gaseous hydrocarbons, carbon monoxide and absorbed soluble organic fraction of the exhaust without increasing the mass of the particulate emissions arising from the formation of sulphates.

Catalyst development was conducted using Engine B fitted to a stand dynamometer (20). The catalysts were evaluated under steady state conditions, using engine load to control the operating temperature. This test was conducted at 2500 RPM using fuel with 0.16 weight per cent sulphur. The system was stabilised at each test point prior to exhaust sampling. Baseline emissions were measured at each temperature, with an uncatalysed substrate in the exhaust system to equalise back-pressure on the engine.

The data in Figure 4 represents the baseline particulate analyses as a function of engine load. For Engine B, which generates a “dry” particulate, with increasing load the soluble

organic fraction remains approximately constant while the carbon and sulphate fractions increase. Figure 5 gives the particulate formation rate when a standard platinum oxidation catalyst is placed in the exhaust system. Excellent removal of the soluble organic fraction is observed with little impact on the “hard” car-

Space Velocity:	42,000 per hour
Catalyst Size:	1.0" dia × 2.33" long
Gas Flow Rate:	20.0 SLPM
Gas component	Concentration
C <sub>10</sub> H <sub>22</sub>	1000 ppm (C <sub>1</sub> )
NO <sub>x</sub>	400 ppm
CO	200 ppm
SO <sub>2</sub>	50 ppm
O <sub>2</sub>	12.0 %
CO <sub>2</sub>	4.5 %
H <sub>2</sub> O	4.5 %
N <sub>2</sub>	Balance

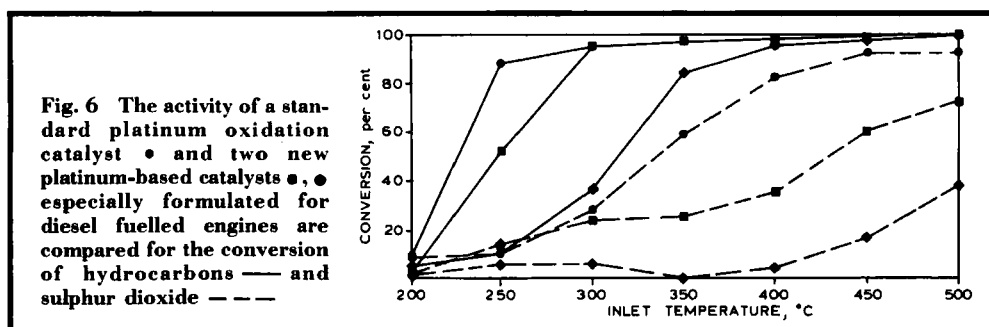


bon particulate, however, above 300°C progressively larger quantities of sulphate are formed. In spite of the removal of the soluble organic fraction over the catalyst there is actually a large net increase in particulate formation, due to the oxidation of sulphur dioxide and the formation of sulphuric acid.

In view of the clear requirement for reduced sulphur dioxide oxidation, new platinum-based diesel catalyst formulations were developed to reduce the oxidation of sulphur dioxide to sulphur trioxide and to limit the degree of sulphur storage on the catalyst surface. Initial evaluation of developmental catalysts was performed utilising a synthetic gas mixture. Since

hydrocarbons in the soluble organic fraction are typically of high molecular weight, decane ( $C_{10}H_{22}$ ) was added to the feed-gas to model the hydrocarbon oxidation requirements of a diesel catalyst. The relevant experimental conditions are given in Table V. Hydrocarbon conversion was measured by flame ionisation detection while sulphur dioxide conversion was monitored by gas chromatography. The test results are given in Figure 6 and show a decrease in sulphur dioxide conversion with the new catalyst formulations. This lower activity is accompanied by a decrease in hydrocarbon oxidation activity.

These new catalyst formulations were then





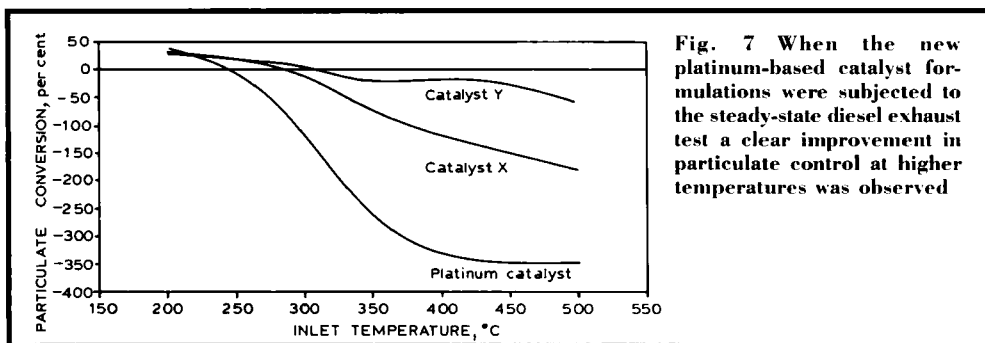


Fig. 7 When the new platinum-based catalyst formulations were subjected to the steady-state diesel exhaust test a clear improvement in particulate control at higher temperatures was observed

evaluated on Engine B utilising the steady-state diesel exhaust test. An obvious improvement in higher temperature particulate control was observed. However, as predicted in the synthetic gas test, low temperature hydrocarbon activity was somewhat reduced. Dynamometer data for particulate and hydrocarbon conversions are given in Figures 7 and 8, respectively. Significant removal of particulate can be achieved by designing the catalyst to minimise sulphate emissions and prevent fouling by rapid carbon accumulation. Some compromise must be made for gas phase hydrocarbon activity. Although, meeting standards for gas phase hydrocarbon emissions is typically not difficult, some further improvement may be desirable for European light-duty vehicles which must meet a hydrocarbon + nitrogen oxide standard. This is the focus of future efforts in this area.

## Conclusions

The development of platinum-based catalysts for the control of diesel engine exhaust requires

a knowledge of the exhaust temperature and the particulate composition. Although these factors are dependent upon individual engine design, the catalyst may be tailored to meet specific requirements.

To meet new regulatory standards a reduction in exhaust particulates is required and the key to achieving this is by the control of sulphur dioxide oxidation. Some compromise in gas phase hydrocarbon activity may be required to obtain the necessary reduction in the formation of sulphuric acid. New platinum-based catalysts have been developed to lower sulphur dioxide oxidation while at the same time minimising fouling of the catalyst due to carbonaceous soot. Thus particulate reduction is achieved primarily by efficient catalytic removal of the soluble organic fraction of the particulate.

## Acknowledgment

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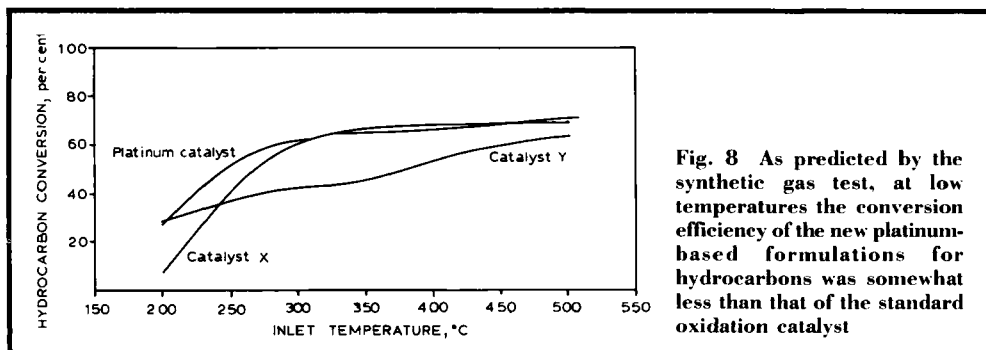


Fig. 8 As predicted by the synthetic gas test, at low temperatures the conversion efficiency of the new platinum-based formulations for hydrocarbons was somewhat less than that of the standard oxidation catalyst

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## Royal Commission Report on Diesel Emissions

The impact of diesel emissions on the environment and methods for their control have been studied by the Royal Commission on Environmental Pollution, of the United Kingdom. On 4th September 1991, they published their report entitled "Emissions from Heavy Duty Diesel Vehicles". The main recommendations to and conclusions for H.M. Government are:

Diesel vehicles are major contributors of atmospheric nitrogen oxides, which have adverse health effects and cause ozone formation, and of particulates which are probably carcinogens and which cause major soiling of buildings.

The Commission recommends that further reductions in both nitrogen oxides and particulates should be sought before the end of the decade. They also recommend that the European Community's steady state test cycle, during which emissions are measured against the standards set, should be made more demanding and along the lines of the U.S. Government's transient test cycle, and that financial incentives should be created to encourage the use of engines with lower emission levels and to speed the replacement of vehicles and engines with new, less polluting ones.

The report also recommends that, as a matter of urgency, H.M. Government should start trials of "traps" or flow-through catalysts to catch particulates, providing grants for retrofitting them to buses, if the trials are successful. Emissions should be lower in urban areas so tighter limits should be set for vehicles

operating in these areas, such as buses. The report suggests that this would require the fitting of particulate traps and flow-through catalysts. [These would probably be based on platinum group metals].

Incentives should be created to subsidise the costs of an early introduction and the use of low sulphur fuel (0.05 per cent), and Government should encourage bus operators to use alternative fuels such as petrol, liquified petroleum gas, compressed natural gas or electricity.

Usefully, the report encourages Government to study the implications of the production and use of such fuels upon emissions of carbon dioxide and other pollutants, balancing the widespread view that carbon dioxide emissions are the only gas from motor vehicles that have implications for global warming. The report recommends that the use of metallic fuel additives should be banned until the exhaust products have been checked with toxicological testing. If a trap or catalyst is fitted, it is the exhaust leaving the device which should be tested.

The report provides further encouragement to H.M. Government to support tougher emissions legislation for diesel engines. In Europe an increasing number of carmakers are offering diesel vehicles equipped with platinum group metal catalysts, which result in substantially cleaner emissions than the 1992 European regulations stipulate for carbon monoxide and hydrocarbons.

R.A.S.