Control of Nitrogen Oxide Emissions from Automobile Engines

THE DEVELOPMENT OF RHODIUM/PLATINUM THREE-WAY CATALYST SYSTEMS

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Regulations requiring strict control of nitrogen oxide emissions from automobiles come into force in 1981 in the United States. This has necessitated the development of new catalyst systems that are capable of controlling nitrogen oxide as well as hydrocarbon and carbon monoxide emissions from spark ignition engines. These devices are known as three-way catalysts. Johnson Matthey have developed catalyst systems based upon platinum and rhodium to meet the requirements and these have been certified for use on 1981 model year vehicles by a number of automobile manufacturers.

The pollution of the atmosphere by the gasoline engine was first observed in Los Angeles and then later in Tokyo in the form of photochemical smog. This phenomenon, illustrated in Figure 1, is caused by the interaction of nitrogen oxides and hydrocarbons in sunlight to form lachrymatory compounds that cause impairment to health and damage to vegetation (1, 2). Climatic conditions in Los Angeles and Tokyo retard the dispersion of these pollutants, although the problem is by no means confined to these cities. Exhaust gases from motor vehicles account for as much as 90, 60 and 40 per cent of man-made carbon monoxide, hydrocarbon and nitrogen oxide emissions, respectively.

Growing concern with the contribution by the car to the pollution of the environment has resulted in increasingly severe worldwide automobile emission legislation, with the strictest controls being imposed in the United States and Japan.

Emission Legislation

The U.S. emission legislation is summarised in Table I, where it can be seen that the permissible emissions of hydrocarbons, carbon monoxide and nitrogen oxides from motor vehicles are being progressively reduced. In particular, the legislation governing nitrogen oxide emissions for 1981 model year vehicles requires very much closer control of this pollutant compared with previous years. This has necessitated the development of advanced control technology to allow vehicles to meet the relevant standard.

Exhaust emissions are measured over a driving cycle that simulates a typical urban driving schedule, and the exhaust gas is continuously sampled and collected while the

Fig. 1 The pollution of the atmosphere by the gasoline engine was first observed in Los Angeles in the form of photochemical smog. This is seen from a distance as a yellow-brown layer in the atmosphere above the city and is caused by the interaction of nitrogen oxides and hydrocarbons in the sunlight to form lachrymatory compounds. Climatic conditions retard the dispersion of these pollutants

vehicle is driven on a rolling road dynamometer, see Figure 2. The gases collected are analysed for hydrocarbons, carbon monoxide and nitrogen oxides and the results are expressed as grams per mile emissions. In the U.S.A. this is known as the C.V.S., constant volume sampling, test. Emission control devices must be effective in meeting the legislated standards for a minimum of 50,000 miles of road use.

Emission Control Technology

The variation in engine exhaust emissions is shown in Figure 3, where pollutant concentration is plotted against equivalence ratio (λ); this being the ratio between the air : fuel ratio at a particular point and the air : fuel ratio at stoichiometry. The actual air to fuel ratio (A/F) at stoichiometry is dependent on fuel composition but is generally considered to be around 14.6, where the value of $\lambda = 1$. If the engine is tuned rich of stoichiometry, hydrocarbon and carbon monoxide emissions are high, nitrogen oxide emissions are low and the oxygen content of the exhaust is minimal. As the engine tune is moved towards stoichiometry, hydrocarbon and carbon monoxide emissions fall but nitrogen oxide emissions rise to a maximum just lean of stoichiometry. In practice, engine emissions

Table I
Legislation Governing Automobile Emissions in the United States of America

Model year	Emission limits, grams per mile		
	Hydro-carbons	Nitrogen oxides	Carbon monoxide
U.S. Federal Emission Limits			
1970	4.1	4.0	34
1975	1.5	3.1	15
1980	0.41	2	7
1981	0.41	1	7
Californian Emission Limits			
1977	0.41	1.5	9
1981	0.41	0.7	7

Fig. 2 A vehicle is driven on a rolling road dynamometer over a driving cycle that simulates a typical urban driving schedule and exhaust gas is continuously sampled and collected. The gases collected are analysed for hydrocarbons, carbon monoxide and nitrogen oxides. This is known as the C.V.S. test and is used to assess the ability of a vehicle to meet legislated standards over 50,000 miles

vary substantially according to operating conditions and control devices must be designed to cope with these variations.

All methods aimed at reducing pollutant levels to meet legislation are designed to give the best possible exhaust gas quality, with the smallest possible reduction in vehicle performance, for example fuel consumption and driveability. The main problem in this respect relates to the opposing concentrations of hydrocarbons and carbon monoxide on the one hand and nitrogen oxides on the other, which are a function of λ. Prior to 1975 a combination of mechanical techniques, such as lean idle, spark retard, exhaust gas recirculation (E.G.R.), together with thermal reactors was capable of meeting legislation, often at some cost to fuel consumption and driveability. In 1975, legislation became so severe that mechanical devices could no longer practically meet the requirements. Then automobile exhaust catalysts were introduced, and these not only enabled closer control of emissions but also allowed engines to be retuned for greater fuel economy.

Early emission legislation required little control of nitrogen oxides, and an oxidation catalyst was used to regulate both hydrocarbons and carbon monoxide. Oxidising conditions at the catalyst were ensured by supplying excess air from an air pump or Pulsair system (3). A small degree of nitrogen oxide control was achieved by exhaust gas recirculation. Exhaust catalysts are poisoned by lead (4) and hence it was necessary for lead free fuel to be introduced into the U.S.A., also in 1975. Catalysts are typically supported upon ceramic monoliths or alumina pellets and the former are wash coated with an alumina layer prior to impregnation with a noble metal catalyst.

The Johnson Matthey Group has been involved in the development of ceramic monolith supported catalysts since the early seventies and was among the first to demonstrate the viability of such systems on automobiles (5). Since the introduction of catalysts to meet the legislation in 1975 model year, the Johnson Matthey Group has supplied over 9 million units to the motor industry world-

wide. The noble metal most commonly used in exhaust catalysts is platinum, but this is usually promoted by a second noble metal, generally palladium or rhodium. Palladium/platinum is the most frequently used combination in present oxidation catalysts, although pure platinum and rhodium/platinum are also used in certain applications.
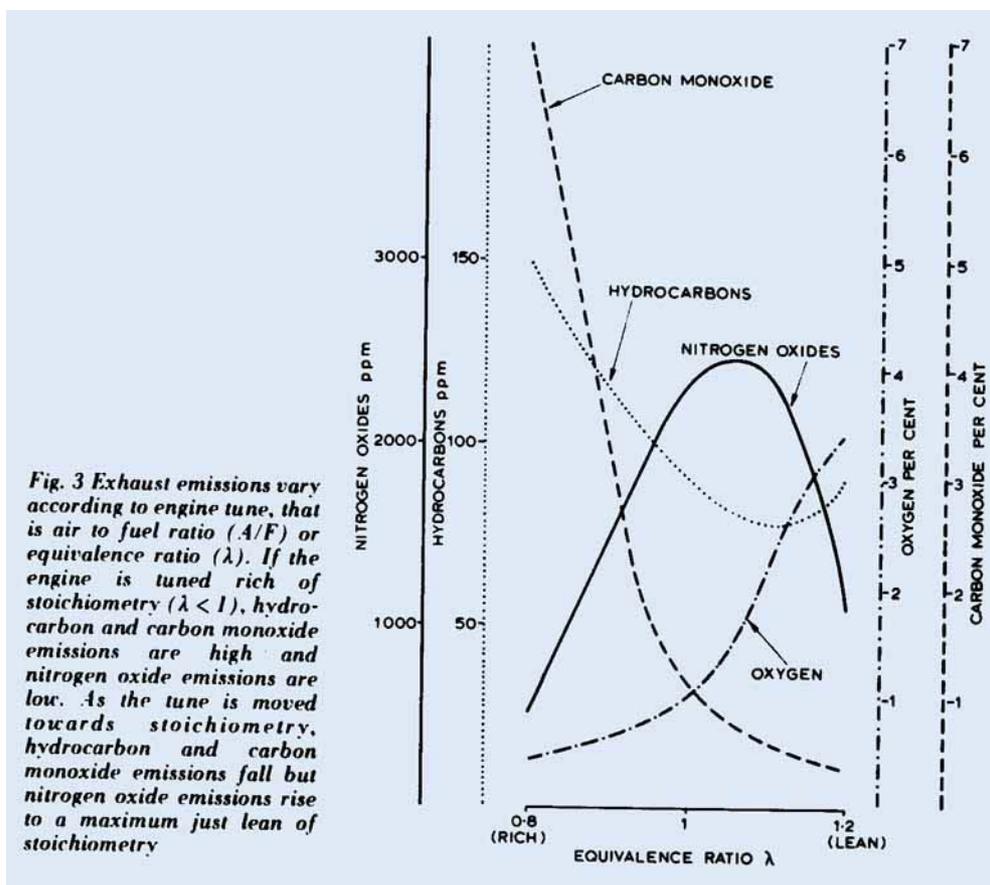
Three-Way Catalysts

The progressive tightening of emission legislation has culminated in 1981 in the necessity to control nitrogen oxides by a method other than E.G.R. since over-application of this technique results in increased fuel consumption and poorer driveability.

The Johnson Matthey Group has played a leading role in the development of catalysts which are capable of removing hydrocarbons, carbon monoxide and nitrogen oxides simultaneously—hence they are known as three-way catalysts—according to the following generalised reactions:

$$2CO + 2NO \longrightarrow 2CO_2 + N_2$$
$$HC + NO \longrightarrow CO_2 + H_2O + N_2$$
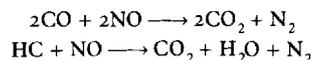
In the development of these catalysts it was necessary to identify additives which were capable of adsorbing and promoting the removal of nitrogen oxides under carefully controlled conditions such that the emissions reaching the catalysts were close to reaction stoichiometry. The most promising of these promoters were ruthenium and rhodium (5), which both showed high activity and selectivity, when combined with platinum, in converting nitrogen oxides to harmless nitrogen. Unfortunately, ruthenium possesses a volatile

Fig. 3 *Exhaust emissions vary according to engine tune, that is air to fuel ratio (A/F) or equivalence ratio (λ). If the engine is tuned rich of stoichiometry (λ < 1), hydrocarbon and carbon monoxide emissions are high and nitrogen oxide emissions are low. As the tune is moved towards stoichiometry, hydrocarbon and carbon monoxide emissions fall but nitrogen oxide emissions rise to a maximum just lean of stoichiometry*

oxide, ruthenium tetroxide, which is formed on the catalyst during the lean excursions that occur even with the best fuel management systems. Thus while ruthenium/platinum catalyst systems gave high initial activity, this performance deteriorated on ageing due to loss of ruthenium. Hence all three-way catalysts are now based on a rhodium/platinum system that does not suffer the same volatility problem.

The selectivity or operating characteristic of a rhodium/platinum catalyst is shown in Figure 4, where catalyst conversion efficiency is plotted against equivalence ratio, λ. In order to remove hydrocarbon, carbon monoxide and nitrogen oxide emissions on a single catalyst, it is obvious that the emissions reaching the catalyst must be controlled close to stoichiometry, where the value of λ is 1. If $\lambda < 1$, the control of nitrogen oxides is effective but the removal of carbon monoxide and hydrocarbons is poor because of the lack of oxidants. If $\lambda > 1$ control of nitrogen oxides is lost, because the preferential adsorption of oxygen on the catalyst surface makes the catalyst function as an oxidation system. Thus the "operating window" of a true three-way catalyst is confined to a fairly narrow range of λ values.
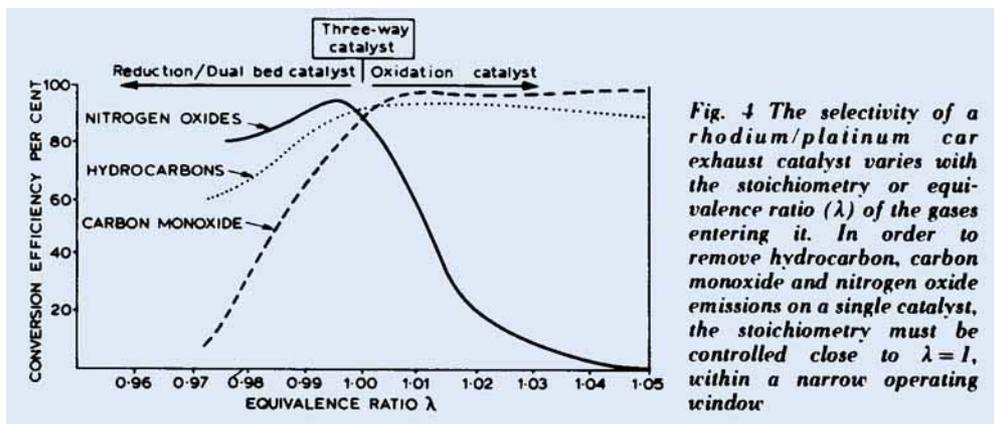
The stoichiometry of the emissions reaching the catalyst can be controlled by a closed loop feedback system incorporating an oxygen or λ sensor. The sensor is an oxygen concentration c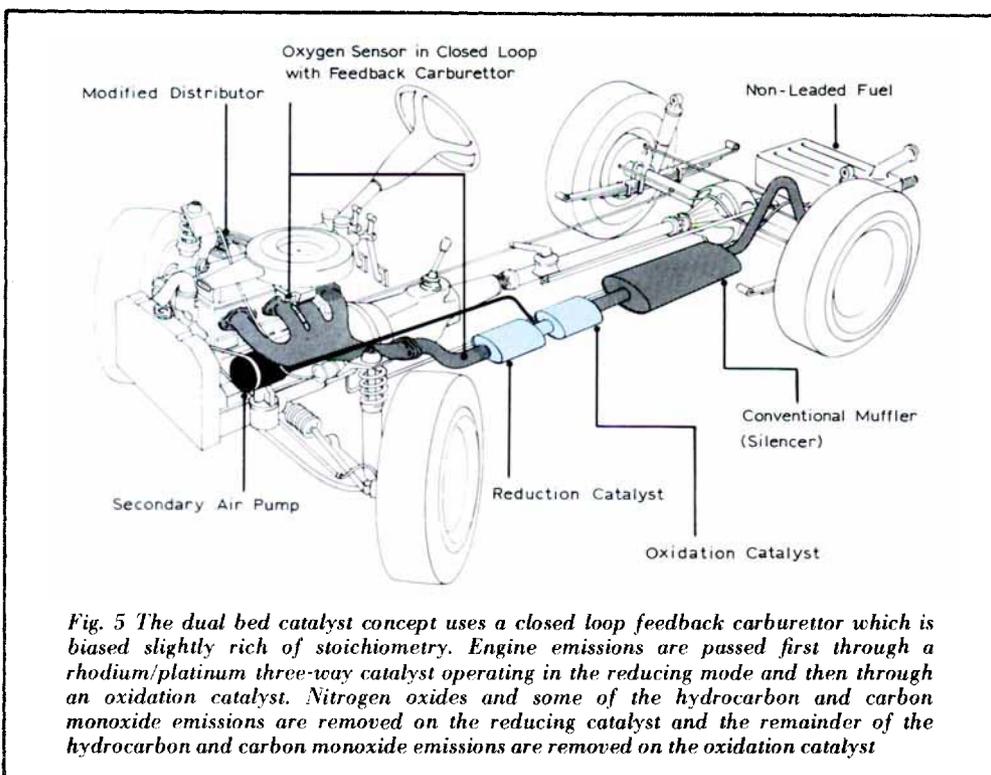ell with an oxygen ion conducting solid electrolyte which provides a sharp voltage step at the stoichiometric air to fuel ratio (6). This signal, after processing in an electronic control unit, is used to regulate the fuel management system and thus provide a stoichiometric gas composition to the catalyst.

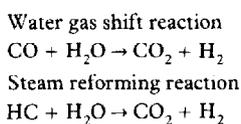## Catalyst Systems for 1981 Model Year Automobiles

The Dual Bed System

The fuel metering system used on the great majority of mass produced vehicles is the carburettor. Hence, in order for a three-way catalyst to operate satisfactorily, it is necessary to control the air-fuel output of the carburettor by an oxygen sensor. This is often done by using the sensor signal to operate motorised fuel or air intakes. However, because the carburettor is a relatively crude method of metering fuel, it is difficult to control λ sufficiently close to stoichiometry for a single three-way catalyst to be used satisfactorily. In practice, it is common to find fluctuations or "perturbations" of up to ± 1 A/F ($\lambda = \pm 0.07$) at a frequency of one cycle per second in a closed loop feedback carburettor system. A further examination of Figure 4 reveals that the operating window of a rhodium/platinum three-way catalyst is too narrow to permit acceptable operation under such widely fluctuating conditions. With this type of fuel management system, therefore, a different catalyst concept—known as the dual bed concept—

Fig. 4 *The selectivity of a rhodium/platinum car exhaust catalyst varies with the stoichiometry or equivalence ratio (λ) of the gases entering it. In order to remove hydrocarbon, carbon monoxide and nitrogen oxide emissions on a single catalyst, the stoichiometry must be controlled close to $\lambda = 1$, within a narrow operating window*

Fig. 5 The dual bed catalyst concept uses a closed loop feedback carburettor which is biased slightly rich of stoichiometry. Engine emissions are passed first through a rhodium/platinum three-way catalyst operating in the reducing mode and then through an oxidation catalyst. Nitrogen oxides and some of the hydrocarbon and carbon monoxide emissions are removed on the reducing catalyst and the remainder of the hydrocarbon and carbon monoxide emissions are removed on the oxidation catalyst

must be used for effective emission control.

The dual bed catalyst concept is illustrated in Figure 5 and employs a closed loop feedback carburettor which is biased slightly rich of stoichiometry. The emissions are passed first through a three-way (rhodium/platinum) catalyst operating in the reducing mode and then through an oxidation catalyst. Air is injected into the exhaust system between the two catalysts. Thus much of the nitrogen oxides and some of the hydrocarbons and carbon monoxide are removed on the reducing catalyst and the remainder of the hydrocarbons and carbon monoxide is cleaned up on the oxidation catalyst. Under these circumstances, other potential reactions must be considered, particularly on the rich side of stoichiometry, for example:

Water gas shift reaction
$$CO + H_2O \rightarrow CO_2 + H_2$$
Steam reforming reaction
$$HC + H_2O \rightarrow CO_2 + H_2$$

Thus, there is the possibility of improving rich side hydrocarbon and carbon monoxide conversion by adding water gas shift and steam reforming components to the three-way catalyst formulation. There is, however, also a chance of ammonia formation on the three-way catalyst under rich conditions:

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$$
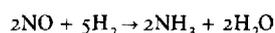
The ammonia would then be re-oxidised to nitrogen oxides on the clean-up oxidation catalyst yielding little overall benefit.

The three-way catalyst formulation can be chosen to minimise ammonia formation. For example, rhodium is used in three-way catalysts because of its ability to convert nitrogen oxides to nitrogen selectively. The effect of rhodium loading on ammonia formation for a Pt/Rh catalyst formulation is shown in Figure 6, where increasing the rhodium loading decreases ammonia formation.

A further phenomenon associated with three-way catalysts is that of "oxygen storage" (7). The width of the catalyst operating window on
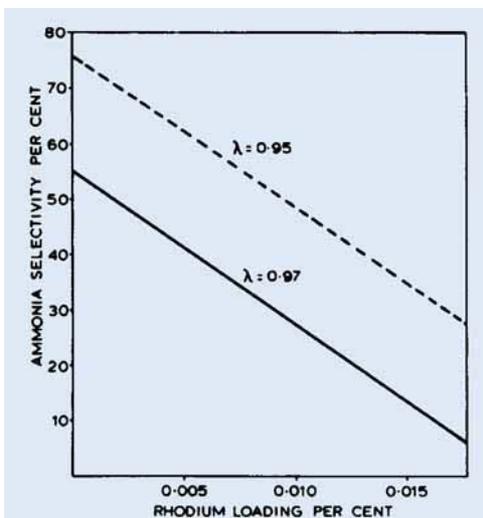
Fig. 6 The formation of ammonia under rich conditions (λ < 1) on a three-way catalyst can be minimised by using rhodium in the formulation. Rhodium has the ability to convert nitrogen oxides to nitrogen selectively, and ammonia formation is dependent upon the loading of rhodium in the catalyst

the lean side is limited by the preferential adsorption of oxygen on the catalyst surface with a concomitant loss in nitrogen oxide conversion. In theory, an oxygen storage component is capable of preferentially removing oxygen from active catalyst sites during lean excursions and releasing it again during rich excursions. Thus the inclusion of an oxygen storage component in a three-way catalyst broadens the operating window under fluctuating A/F ratio conditions.

It can be seen from the above that a three-way catalyst is far from simple and must be optimised to perform a number of functions. The overall activity and light-off performance is related to the noble metals used, their dispersion and their position within the catalyst (8, 9). The range of operation of a three-way catalyst can be improved by the addition of oxygen storage, water gas shift, steam reforming and ammonia decomposition components.

Three-way catalysts have been under development within the Johnson Matthey

Group for several years. Indeed, one customer, Volkswagen, has been using an open loop fuel injection system with a rhodium/platinum catalyst since 1975 (10). Although this is basically an oxidation system a small degree of nitrogen oxide control is achieved during rich excursions.
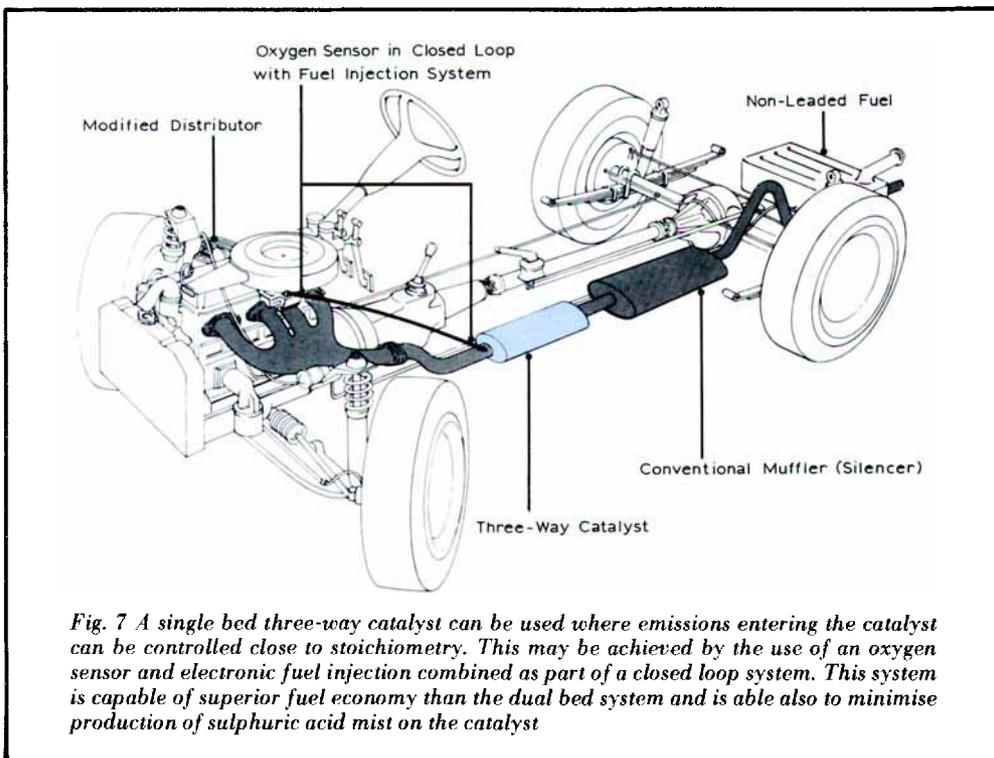
Prior to evaluation by customers, Johnson Matthey catalyst systems are tested by ageing on static engine dynamometers over an accelerated ageing cycle for 300 hours to simulate the accumulation of a high road mileage. After ageing, catalysts are evaluated on vehicles against the C.V.S. test. The results of such tests, performed on a 2.3 litre Ford Pinto car fitted with a closed loop feedback carburettor system, are shown in Table II. The result for the three-way catalyst alone demonstrates the difficulty in meeting the emission standards using a single catalyst with this type of fuelling. However, when the vehicle is fitted with a three-way catalyst as part of a dual bed system, the 1981 emission standards are achieved comfortably even with aged catalysts.

The Single Bed System

Many European car manufacturers who export to the United States and to Japan

Table II
C.V.S. Test Results on an Aged (300 hours) Three-Way Catalyst on a 2.3 Litre Ford Pinto Car Equipped with a Closed Loop Feedback Carburettor

	Emission levels, grams per mile		
	Hydro-carbons	Nitrogen oxides	Carbon monoxide
Single three-way catalyst	0.68	0.92	9.29
Three-Waycatalyst + oxidation catalyst (Dual bed)	0.27	0.85	2.02
1981 U.S. Federal Emission Limits	0.41	1.0	7.0

Fig. 7 *A single bed three-way catalyst can be used where emissions entering the catalyst can be controlled close to stoichiometry. This may be achieved by the use of an oxygen sensor and electronic fuel injection combined as part of a closed loop system. This system is capable of superior fuel economy than the dual bed system and is able also to minimise production of sulphuric acid mist on the catalyst*

incorporate fuel injection as standard equipment. Fuel injection is an accurate method of fuel metering which, in combination with an oxygen sensor in a closed loop feedback system, is capable of controlling the emissions entering the catalyst close to stoichiometry. A typical perturbation amplitude and frequency for this system is ±0.25 A/F ($\lambda = \pm 0.02$), at one cycle per second, which is sufficiently close to stoichiometry to allow the use of a single bed three-way catalyst system, the arrangement of which is shown in Figure 7. Further advantages of this system are that, because it can be tuned close to stoichiometry, it is capable of better fuel economy than the dual bed system and there is less chance of sulphur dioxide in the feedstream converting to sulphur trioxide and hence sulphuric acid mist (11). Much of the chemistry applied to the development of three-way catalysts for dual bed operation also applies in the case of single bed units, since many of the problems remain the same, albeit reduced by the accuracy of the fuelling system. Results

obtained on an aged single bed three-way catalyst on an Audi Fox 1.6 litre vehicle fitted with a closed loop fuel injection system are shown in Table III. While it is not strictly fair to make a direct comparison with the results

Table III

C.V.S. Test Results on an Aged (300 hours) Three-Way Catalyst on a 1.6 Litre Audi Fox Car Equipped with a Closed Loop Fuel Injection System

	Emission levels, grams per mile		
	Hydro-carbons	Nitrogen oxides	Carbon monoxide
Single three-way catalyst	0.29	0.53	3.53
1981 U.S. Federal Emission Limits	0.41	1.0	7.0

obtained for the dual bed system on the Ford Pinto, Table II, it is apparent that the vehicle fitted with the fuel injection system is able to meet the 1981 emissions legislation with a single bed three-way catalyst.

Conclusion

Johnson Matthey catalysts for both single bed and dual bed applications have now been certified for use by a number of U.S. and European car manufacturers to meet 1981 U.S. legislation. While it is not yet clear how U.S. legislation may be changed in the future, the development of three-way catalysts within the Johnson Matthey Group is continuing with the aims of improving overall activity and durability and of improving the effectiveness of both the noble metal and the base metal components of the system.

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The 1980 MacRobert Award

PLATINUM CATALYSTS FOR THE CONTROL OF EXHAUST EMISSIONS

The highly regarded MacRobert Award, consisting of a gold medal and a cash prize of £25,000, has been made to a small team from the Johnson Matthey organisation for their outstanding work on the development and exploitation of platinum group metal catalyst systems for the control of motor vehicle exhaust emissions. Lord Robens, Chairman of the Company, received the Award from H.R.H. The Duke of Edinburgh, the Senior Fellow of the Fellowship of Engineering, at a private ceremony held at Buckingham Palace on December 16th, 1980.

The Award was instituted in 1968 and is made annually now by the Fellowship of Engineering, on behalf of the MacRobert Trusts. It aims to honour individuals or small teams who have made an outstanding contribution by way of innovation in engineering or the other physical technologies, or in the application of the physical sciences, which has enhanced, or will enhance, the prestige and prosperity of the United Kingdom.

In 1970, when the United States of America introduced legislation aimed at reducing substantially the exhaust emissions from motor vehicles, Johnson Matthey was actively engaged in improving catalyst technology. It had already successfully developed and marketed new catalyst systems for the control of air pollution emitted from industrial processes, using ceramic honeycomb supports and mixed platinum metal catalysts. The pollutant gases present in vehicle emissions, carbon monoxide, nitrogen oxides and hydrocarbons, could each be rendered innocuous under carefully controlled conditions. However, the catalysts available at the time did not possess the activity, selectivity or durability to achieve the necessary standards in the widely differing conditions prevailing in a motor vehicle exhaust for the minimum required life of 50,000 miles.

Following intensive research and development, Johnson Matthey succeeded in producing a system to satisfy the requirements of U.S. legislation. In addition Johnson Matthey undertook to manufacture and market these catalyst systems. In order to serve both the European car manufacturers exporting to the U.S.A. and the big American manufacturers, production facilities were set up in both the U.K. and U.S.A. These were built to manufacture up to five million catalyst units per year, and have been modified since to incorporate the latest technology, thus enabling Johnson Matthey to provide a range of motor vehicle emission control catalysts that have progressively met the increasingly stringent legislation in the U.S.A.