# **Automobile Emission Control** Systems

# PLATINUM CATALYSTS FOR EXHAUST PURIFICATION

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Stringent regulations governing automobile exhaust emissions are due to come into force in the United States. Johnson Matthey have undertaken the development of platinum-based catalytic reactors for control of these exhaust emissions. Two new types of catalyst have demonstrated the feasibility of exhaust control by catalytic means, and have been incorporated on test vehicles to achieve emission levels well below the specified levels for 1975 and 1976 model year cars. Extended road mileage on the former system has shown that good durability can be obtained, with emissions below 1975 limits for 25,000 miles.

The world-wide concern over environmental pollution with respect to the gasoline engine began in the early 1940s when Los Angeles residents became aware of an atmospheric phenomenon known as photochemical smog. Studies (1, 2) showed that the smog formation resulted from reaction between nitrogen oxides and hydrocarbons, producing harmful lachrymatory compounds. These were retained in the Los Angeles basin by a temperature inversion in the upper atmosphere preventing dispersion of the pollutants, causing smog formation. Although Los Angeles represents a specific problem due to climatic conditions peculiar to the area, the smog formation focused attention in the United States on all aspects of atmospheric pollution. A major source of pollution was shown to be the internal combustion engine (3) which produces principally carbon monoxide (CO), hydrocarbons (HC), nitric oxide (NO), with small amounts of sulphur oxides (SO<sub>x</sub>), lead (Pb) and particulates. One source of American data (4) quotes the contribution of the automobile to atmospheric pollution as high as: CO 90 per cent, HC 65 per cent and NO<sub>x</sub> (nitrogen oxides) 60 per

cent. The figures are of course extremely variable from country to country, the American figure being one of the highest, and virtually depend on the immediate environment of the test. However, the figures reflect the concern over the automobile's contribution to pollution, not only in the Los Angeles area, but also in conurbations where high traffic density occurs.

As a result, increasingly severe legislation has been laid down (initially in California but extending to the rest of the United States) to limit noxious emissions from automobiles. This culminated in the signing of the 1970 Clean Air Amendments Act which calls for 90 per cent reduction of CO and HC emissions from 1970 model year levels by 1975, and 90 per cent reduction of NO<sub>x</sub> emissions from 1971 model year levels by 1976.

## U.S. Federal Legislation **Governing Automobile Emissions**

The increasing severity of emission regulations is shown in Table I which gives the permissible levels of exhaust emissions (CO, HC, NO<sub>x</sub>) together with evaporative and



Fig. 1 The Johnson Matthey exhaust catalysts consist of promoted platinum metals supported on a ceramic honeycomb. The catalyst is housed in a stainless steel reactor similar in size and shape to a conventional silencer. Both elliptical and cylindrical units of various sizes are produced, depending on the space beneath the vehicle to be fitted and on the capacity of the engine on that vehicle

particulate emission standards. The relative importance of exhaust emission control is reflected in the following figures, which represent the sources of pollution on a car:

Crankcase	20%
Carburettor	<b>9</b> %
Fuel Tank	6%
Exhaust	65%

and further discussion will concentrate on this aspect.

Exhaust emission levels for 1972 model year onwards are measured over a complex driving cycle of 23 minutes duration simulating urban traffic conditions (Fig. 2), the test being carried out with the vehicle on a roller dynamometer facility. The exhaust is collected from the point when the engine starts to when it stops by constant volume sampling (CVS test). A revised procedure of the CVS test has been introduced for 1975-76 model years incorporating both cold and hot start conditions, a weighted mean of the cold and hot starts being used to calculate the emissions per test in grammes per mile.

U.S. Federal legislation, which is enforced through the Environmental Protection Agency (E.P.A.) also calls for emission control systems

Table I Trends in U.S. Federal Legislation Governing Automobile Emissions					
	CO g/mile	HC g/mile	NO <sub>x</sub> g/mile	Particulate g/mile	Evaporative g/test
1972*	39	3.4		_	2
1973	28	3.0	3.1		2
1975**	3.4	0. <b>4</b> 1	3.1	0.1	2
1976	3.4	0.41	0.4	0.03	2
*Introduction of	CVS test		**Introdu	ction of revised	CVS test



Fig. 2 A Marina test vehicle mounted on a roller dynamometer for the measurement of exhaust emissions over a complex driving cycle simulating urban traffic conditions. During the 23 minutes of the cycle the exhaust is collected by constant volume sampling (CVS test)

to be effective for 50,000 miles road use on a car. The exact interpretation of 50,000 mile durability of emission control components is at the present time a matter of debate but the E.P.A. have the option of allowing replacement of components, such as catalytic reactors, at any mileage interval.

#### **Methods of Emission Control**

Control methods for exhaust emissions can be roughly divided into the two categories of prevention and destruction. Preventive methods have led to the concept of leaner running engines through improved carburetion, distribution and combustion, all of which aid reduction of CO and HC levels. Incorporation of exhaust gas recycling (E.G.R.), where a small proportion of inert exhaust is by-passed to the inlet manifold to dilute the combustion mixture for  $NO_x$ control, forms the pattern of emission control system up to model year 1974.

The increasing severity of emission limits in 1975 and 1976 has forced automobile companies to concentrate on post-combustion treatment of exhaust gases by destructive methods such as manifold air oxidation (Man Air Ox), thermal reactors, and catalytic reactors, and some combination of preventive and destructive techniques will form the optimum emission control package for these years.

Of the available destructive means, catalytic reactors are the most favoured because of their high efficiency at low operating temperatures, and the relatively few modifications required for their installation. Manifold air oxidation systems, aimed at reacting residual CO and HC in the hot exhaust manifold, suffer due to limited efficiency, and thermal reactors, aimed at reacting pollutants at high temperature, require high thermal efficiency and expensive reactor components. On the other hand, catalytic reactors can be designed to operate at typical exhaust temperatures, with high conversion efficiency, thus negating the need for expensive reactor components, although stainless steel exhaust systems and reactors are required for 50,000 mile durability.

Previous attempts at catalytic purification of exhaust gases have been thwarted by the use of lead (anti-knock) and phosphorus (preignition control) compounds in the fuel, since these compounds can rapidly poison catalysts. However, these compounds have been recognised as harmful pollutants, with the result that E.P.A. has called for progressive phasing out of their use by 1975. This involves redesign of engines to cope with lower octane fuels, but advances in petroleum refining using "Platforming" catalysts, recently reviewed in this journal (5), will vastly contribute to the need for high octane lead-free and phosphorus-free fuel. Thus the way is now clear for catalytic reactors to form a viable part of the emission control concept.

#### **Catalytic Exhaust Purification**

The aim of catalyst systems is to remove CO and HC by oxidation to  $CO_2$  and water, and to remove  $NO_x$  by either reduction to  $N_2$  or by decomposition to  $N_2$  and  $O_2$ . Unfortunately simple  $NO_x$  decomposition

catalysts are far too ineffective to be used in a car exhaust reactor, the weight of catalyst required being prohibitive. However, the reduction of  $NO_x$  by the CO or HC present in the exhaust is a much faster reaction, allowing a viable reactor design.

The oxidation and reduction mechanisms involved have important implications for the type of emission control system to be used. As a result of this and because the 1976 model year imposes a much greater restriction on permitted NO<sub>x</sub> emission levels, separate systems have had to be developed for 1975 and 1976 models. Up to model year 1975 the required NO<sub>x</sub> emissions can be achieved by E.G.R., and, therefore, for 1975 the preferred system consists of an oxidation catalyst for control of CO and HC emissions and the E.G.R. engine modification for control of NO<sub>x</sub>. For the latter, secondary air is supplied to the exhaust for the catalytic oxidation using a small air pump. (Fig. 3.)



Fig. 3 The Johnson Matthey exhaust emission control system for 1975 model vehicles. Carbon monoxide and hydrocarbons are oxidised in the catalytic converter. Nitrogen oxides are controlled at the required level by the exhaust gas recirculation system



Fig. 4 The Johnson Matthey exhaust emission control system for 1976 model vehicles incorporates two catalytic converter units. The first operates in a nett reducing atmosphere for  $NO_x$  control while the second operates in an oxidising atmosphere to remove carbon monoxide and hydrocarbons. E.G.R. for additional reduction of  $NO_x$  is optional, depending upon engine design parameters

The 1976 emissions requiring lower NO<sub>x</sub> levels cannot be met using E.G.R., as the higher recirculation rate required imposes a severe power loss. Therefore, a second catalyst bed is used for the control of NO<sub>x</sub> and this operates in a nett reducing atmosphere. Air from a pump is fed into the exhaust gas stream after the reduction catalyst. This feeds an oxidation catalyst for the control of the CO and HC emissions. Figure 4 shows the dual bed emission control system for 1976. A significant advantage of Johnson Matthey systems to meet 1976 standards for the catalytic control of CO/HC and NO<sub>x</sub> emissions is their compatibility with the 1975 system, thus reducing engineering costs for modification between 1975 and 1976.

#### **Platinum Catalysts**

The vast experience obtained in the Catalyst Research Department at Johnson Matthey, and at our associate company Matthey Bishop Inc., has shown beyond doubt that the platinum group metals are the most active materials available for control of the type of pollutants produced by the automobile. Previous experience, particularly in organic fume and odour abatement (6, 7), and in nitric acid plant "tail gas" purification requiring  $NO_x$  removal (8), supports this belief.

It is often mistakenly thought that the high intrinsic cost of platinum prohibits its use in automobile exhaust purification. Recent studies at Johnson Matthey in the U.K. and at Matthey Bishop Inc. in the U.S.A., have demonstrated that, due to its high catalytic activity, and as a result of advanced catalyst design, the contribution of the platinum metal is not a significant proportion of the overall cost of the emission control system and this platinum content is sufficient to maintain adequate activity and durability. Thus platinum availability is not a serious problem, providing the automobile manufacturers give sufficient notice of their requirements for proper planning to take place to meet those requirements on an acceptable business basis.

Nevertheless, removal of exhaust pollutants by catalytic means using conventional platinum catalysts is not without its problems. The major difficulties arise in three aspects, namely the temperature of reaction, the chemistry of pollutant abatement, and the durability of the catalyst. The complexity of the problem is further enhanced by the fact that exhaust emissions, reaction temperatures and gas velocities vary widely with carburetted air/fuel ratio and driving mode (idle, acceleration, cruise, and deceleration).

As the 1975 CVS test procedure incorporates a cold start it is imperative that the catalyst becomes effective as soon as possible into the driving cycle, since with earlier catalysts some 90 per cent of the emissions commence within 75 seconds of the choked cold start. To meet the required limits the catalyst must operate preferably within 20 seconds of the cold start and therefore must possess low ignition temperature characteristics. Also catalysts must not operate above their maximum temperature limits, which can easily occur under full load-full speed conditions with poorly designed catalysts, this problem being enhanced by the exothermicity of the oxidative reactions.

The catalysts must be insensitive to air/fuel ratio, i.e. not affected by the relative concentrations of reacting components, and must operate effectively over a very wide range of space velocities (0–150,000 v/vh).

A particular problem prevalent with the reduction catalyst is the tendency of reduction catalysts to produce ammonia as a result of reduction of NO by either the hydrogen present in the exhaust, or hydrogen produced from a catalytic side reaction. Such ammonia is rapidly reoxidised to nitric oxide in the second stage oxidation reactor and thus reduces the nett conversion efficiency of the system for NO.

As previously stated the catalyst should have a life of at least 25,000 miles, and preferably 50,000 miles. This means that the catalyst must be resistant to thermal and mechanical shock, to high temperature conditions caused by engine malfunction, to attrition by high gas flow and particulates, and to trace poisons in the system. Current legislation with respect to the latter has proposed that in gasoline, lead shall not exceed 0.05 g/U.S. gallon and phosphorus shall not exceed 0.01 g/U.S. gallon. These represent a massive reduction from conventional levels but could still present problems when using catalysts for the removal of gaseous emissions.

#### The Advanced Catalyst System

Research in Johnson Matthey has concentrated on solving the specific problems outlined above with respect to exhaust emission control. Test systems such as those shown in Figures 5, 6 and 7 have been employed in the development of catalysts suitable for meeting the proposed emission levels.

Advances made include such features as low ignition temperature, high thermal stability and shock resistance. For example (Fig. 8), the current generation of promoted platinum catalysts show: (a) the ability of oxidation catalysts to convert CO and HC at low exhaust temperatures, and (b) the ability of reduction catalysts to convert NO at low exhaust temperatures while maintaining minimal ammonia formation. The catalytic activity is also insensitive to carburetted air/fuel ratio providing the catalyst is operated in the appropriate oxidising or reducing exhaust stream. Operation of these catalysts at temperatures of 1000°C, typical of engine malfunction, for periods of up to 24 hours has shown no serious loss in performance. Similarly, extended tests on static engines have demonstrated the ability of these catalysts to maintain effectiveness even with trace poisons such as lead and phosphorus present in the fuel and lubricating oil. For example, tests using 0.05 g/gallon leaded fuel, and conventional lubricating oil con-



Fig. 5a

Fig. 5 Front (a) and rear (b) of simulated exhaust test rig at the Johnson Matthey Research Laboratories. The reactor shown in (b) synthesises the components of exhaust gas for preliminary catalyst evaluation tests and for studies of the reaction kinetics involved in exhaust emission control

### Fig. 5b





Fig. 6 (above) A singlecylinder laboratory test engine (left) with its exhaust train (centre). Engines of this type are involved in investigations covering the activity of new catalyst systems, the durability of catalysts and the effects of various catalyst poisons on catalyst life



Fig. 7 A static engine test bed using a two-litre Ford Pinto engine for the evaluation of catalyst performance. The rig is equipped with a cycle programmer for durability tests on the catalyst and its reactor system



Fig. 8 The low temperature activity of Johnson Matthey promoted platinum catalysts. (a) The superior performance of promoted platinum over platinum and over base metal catalysts is seen here for the conversion oxidation of carbon monoxide and hydrocarbons. (b) The promoted reduction catalyst greatly reduces nitrogen oxide emissions while maintaining minimum formation of ammonia

taining 0.070 wt.% phosphorus, have shown very little deterioration in catalyst activity.

As a result two types of catalyst are now produced for automobile exhaust emission control. The CO/HC oxidation catalyst is described by the serial number AEC3A and the NO<sub>x</sub> reduction catalyst by the serial number AEC8A (known in parts of Europe as EC3A and EC8A, respectively). These consist of promoted platinum metals, specifically designed to operate as reductive or oxidative systems and are supported on ceramic honeycomb (Fig. 1). The advantage of the honeycomb support in this system is that it offers low pressure drop, and hence low power loss on an engine, together with low attrition loss, and good thermal mechanical shock resistance.

The catalyst is housed in a stainless steel reactor (Fig. 1) similar in size and shape to a conventional silencer. As the volume of exhaust to be treated is dependent on engine capacity, two basic sizes have been optimised, containing 55 in<sup>3</sup> (900 cm<sup>3</sup>) of catalyst for cars up to 1.5 l and 86 in<sup>3</sup> (1400 cm<sup>3</sup>) of catalyst for catalyst for cars from 1.5 to 2.5 l capacity.

Higher capacities generally use a catalyst unit to treat the exhaust for each bank of cylinders on a V8 or V6 engine. These units are produced in both elliptical and cylindrical configurations to suit the space on the vehicle.

Although laboratory evaluation of the catalytic reactors forms an invaluable feature of our test programme, it would not be complete without the ultimate test against the U.S. Federal Regulations. For this reason Johnson Matthey have equipped two test vehicles with 1975 and 1976 catalytic emission control systems respectively.

#### The 1975 System

A Chrysler Avenger 1500 cc vehicle, equipped with an engine and emission control package to meet 1972 U.S. emission levels has been used as a 1975 test car. This vehicle, which is currently sold in the United States as the Plymouth Cricket, was equipped with a low compression engine possessing induction-hardened valve seats to suit low octane lead-free fuel.

Modifications to this vehicle (Fig. 9a) to meet 1975 emission levels included an E.G.R.





Fig. 9b



Fig. 9 (a) (above) Chrysler Avenger (Plymouth Cricket) engine to meet the 1975 model year U.S. regulations, showing the secondary air pump and exhaust gas recirculation installations.

(b) Beneath this vehicle the CO/HC oxidation catalyst reactor has been installed in the place normally occupied by a silencer (muffler). The standard silencer is further along the exhaust train system recirculating exhaust from the front of the catalyst box to the inlet manifold, and a pump supplying air to the exhaust manifold just above the exhaust valves (Man Air Ox). The E.G.R. system was found suitable for meeting 1975 NO levels when giving about 8 per cent recirculation above 28 m.p.h., and presented no serious power loss problems. The Man Air Ox system, primarily designed to supply air to the catalyst, gave a marginal improvement in baseline CO and HC emissions, which helps prevent over-temperature problems in the catalytic reactor during particular driving modes.

The optimum position for the oxidation reactor was found from exhaust temperature surveys to be under the front passenger seat, and proved opportune for available space since the reactor replaced the front silencer of the existing exhaust system (Fig. 9b). This position proved adequate for the required rapid reactor warm-up as a result of the low ignition temperature of the catalyst, and enabled the oxidation reaction to commence within 20 to 30 seconds of a cold start.

A second aspect of low ignition temperature proved to be the ability to site the reactor

Table II Avenger Test Vehicle Emissions Compared to 1975 Limits			
	CO	HC	NO <sub>x</sub>
	g/mile	g/mile	g/mile
1975 limits	3.4	0.41	3.1
Avenger	0.85	0.11	1.65

away from the exhaust manifold. Although the exhaust manifold is an ideal position for extremely rapid warm-up, it presents serious over-temperature problems at full speed, full load conditions. Thus our low ignition catalysts with high temperature stability enable an optimum position to be established for rapid ignition without over-temperature deactivation.

The Avenger emission control system has been optimised to give the typical exhaust emissions shown in Table II in comparison to the 1975 limits.

Following this work a durability run was commenced, and to date the vehicle has completed 26,500 miles with exhaust emissions remaining within the specified limits.





Fig. 11a

Fig. 11b



Fig. 11 (a) (above) Marina engine to meet the 1976 model year U.S. regulations, showing the secondary air pump and other minor modifications. (b) Beneath this vehicle the  $NO_x$  reduction catalyst reactor is at the top of the picture at the start of the exhaust train. Below it can be seen the oxidation catalyst reactor. The conventional silencer further along the exhaust train is not shown in this picture

Table IIIAvenger Test Vehicle Emissionsbefore Exhaust Treatment			
	CO g/mile	HC g/mile	NO <sub>x</sub> g/mile
Zero miles travelled	8.76	0.76	1.57
26,500 miles travelled	5.81	1.20	2.37

During the test no significant increase was observed in NO and CO emission levels, but HC levels are seen to rise somewhat throughout the test (Fig. 10).

Comparison of untreated exhaust emissions at zero and 26,500 miles (see Table III) has shown a substantial increase in raw hydrocarbon emissions from the engine that in part accounts for the increase in levels throughout the test. (See Fig. 10).

The attainment of over 25,000 miles within 1975 limits using catalytic reactors represents a major contribution to the emission control concept, and demonstrates the feasibility of emission control within the specified limits for 50,000 miles.

#### The 1976 System

Future development of exhaust emission catalysts is now concentrating on the dual bed system for 1976 requirements. A Morris Marina 1800 cc vehicle, with a low compression engine suitable for lead-free fuel, has been equipped with a dual-bed catalytic converter (Fig. 11). An air pump installation similar to that used on the Avenger supplies

Table IVMarina Test Vehicle EmissionsCompared to 1976 Limits			
	CO	HC	NO <sub>x</sub>
	g/mile	g/mile	g/mile
1976 limits	3.4	0.41	0. <del>4</del>
Marina	1.78	0.17	0.25

air to the oxidation catalyst midway between the reduction and oxidation beds. Due to the higher temperatures required for efficient NO reduction (Fig. 8) the first reactor is installed close to the exhaust manifold. This, however, does not create overheating problems, as would be found with an oxidation catalyst in this position, since the heat generated by reaction in this system is minimal. The oxidation catalyst is again installed under the front passenger seat, and, although thermal lag due to the reduction box has been observed during cold starts, the low ignition catalyst has fully coped.

This vehicle is at present completing optimisation trials prior to a 50,000 mile durability run, but has demonstrated that emissions well below the 1976 levels can be achieved using the Johnson Matthey dual-bed catalyst system (See Table IV).

We have demonstrated the technological feasibility of Johnson Matthey catalysts complying with the United States exhaust emission regulations for model year 1975. These catalysts are currently under evaluation by most of the major car companies throughout the world, and further work is in progress to enable car manufacturers to meet the emission regulations by catalytic means.

Further development of these catalyst systems is under way, particularly with respect to the more stringent requirements for model year 1976, and new catalyst formulations offer great promise in those areas where problems remain to be solved.

#### References

- 1 A. J. Haagen-Smit, Ind. Engng. Chem., 1952, 44, 1342
- 2 A. J. Haagen-Smit and M. M. Fox, Ind. Engng. Chem., 1956, **48**, 1484
- 3 L. H. Rogers, J. Chem. Educ., 1958, 35, 310
- 4 R. L. Chass, P. S. Tow, R. G. Lundie and N. R. Shaffer, Air Pollution Control Assn. J., 1960, 10, 351
- 5 E. L. Pollitzer, Platinum Metals Rev., 1972, 16, (2), 42-47
- G. J. K. Acres, Platinum Metals Rev., 1970, 14, (1), 2; Ibid., 1971, 15, (1), 9; Ibid., (4), 132
- 7 G. J. K. Acres, Ibid., 1970, 14, (3), 78
- 8 J. B. Hunter, Ibid., 1968, 12, (1), 2