

Lead Poisoning of Automobile Emission Control Catalysts

THE INFLUENCE OF EMISSION SYSTEM DESIGN

By B. J. Cooper

Group Research Centre, Johnson Matthey & Co Limited

In a paper presented to the American Chemical Society Symposium on Auto Emission Catalysts, held in Chicago in August, an investigation was described in which it was shown that, by careful selection of the position of the catalyst in the exhaust train and of the operating temperature, deterioration due to lead poisoning can be minimised. This article summarises the findings reported in the paper.

The installation of platinum catalysts in an automobile's exhaust train to control carbon monoxide (CO) and hydrocarbon (HC) emissions over a period of 50,000 miles calls for a catalyst system capable of withstanding the many rigours of such a hostile environment. The progressive tightening of U.S. emission standards has caused catalytic researchers to investigate methods of improving catalyst systems for greater control of CO and HC tailpipe emissions. Two factors which control the life of a catalyst system are its ability to withstand high operating temperatures and to withstand poisoning by lead compounds originating from the fuel.

A controversy has recently arisen regarding poisoning by lead, notably from Chrysler (1, 2) who claimed that lead did not poison catalysts if the halide scavenger ethylene dibromide was omitted from the fuel. This claim has been refuted by other workers at Ford (3, 4) and at General Motors (5).

However, since the siting of the catalyst in the exhaust train will control the subsequent environment in which the catalyst operates, elucidation of the poisoning process will be dependent on the installation of the catalyst. Thus the distance from the exhaust manifold,

coupled with the engine tune (amount of CO/HC being burnt over the catalyst) will affect the running temperature of the converter. It will also affect the nature and distribution of lead species deposited on the catalyst surface. The presence of lead scavengers which lead to formation of various lead halide - lead oxyhalide species with a range of volatilities will also affect the lead deposition process.

In an effort to explore these effects, and to resolve the controversy over poisoning rates in the presence and absence of the halide scavenger, Johnson Matthey have conducted a series of tests using monolithic platinum exhaust catalyst described previously (6). These tests determined the relative rates of thermal sintering, and lead poisoning by comparing catalyst performance after 300 hours operation at different engine tune-exhaust position combinations. The aged catalysts were then compared to catalysts poisoned under controlled conditions by a known quantity of lead using an exhaust gas simulator.

Engine Tests

Four EW2/12C/40 catalyst units 4 inches diameter by 6 inches long were aged for

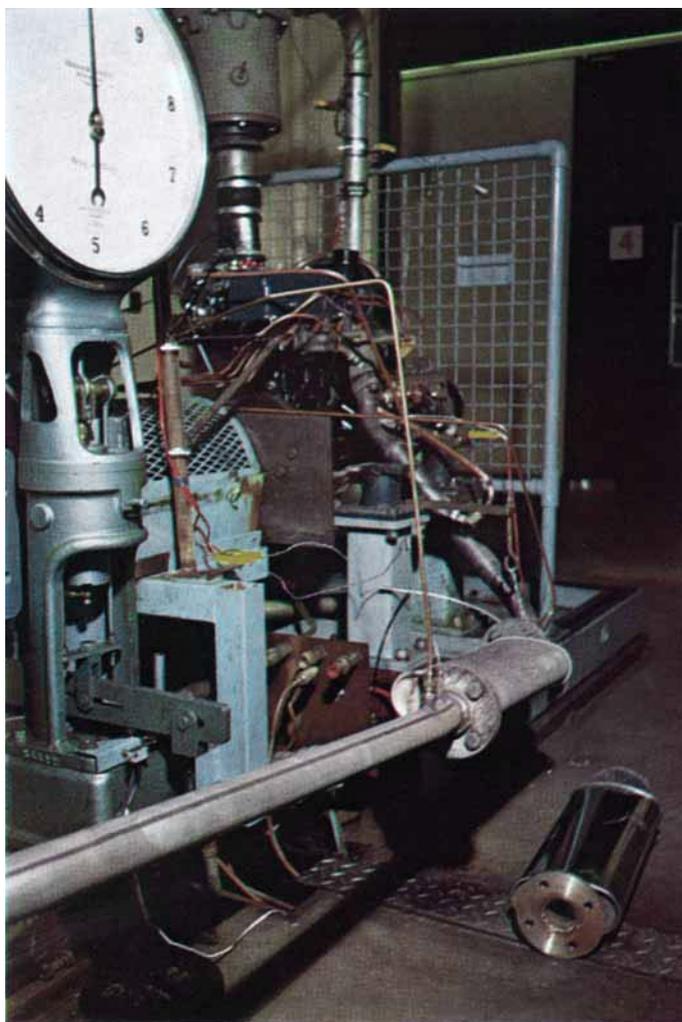


Fig. 1 A static engine test bed for the evaluation of catalyst performance. The rig is equipped with a cycle programmer for durability tests on the catalyst and its reactor system

300 hours in the exhaust train of a 1.8 l Triumph Dolomite Engine. The engine dynamometer shown in Figure 1 is similar to that used for this trial, when fuel containing 0.03 to 0.05 g Pb/U.S. gallon was used.

Conditions experienced by the catalysts in the four positions were as follows:

1. 11 inches from manifold—
outlet temperature 695 to 770°C
2. 11 inches from manifold—
outlet temperature 590 to 660°C
3. 102 inches from manifold—
outlet temperature 615 to 650°C
4. 102 inches from manifold—
outlet temperature 480 to 490°C.

The catalysts were evaluated after ageing for 300 hours by installing them on a slave test car and a slave test engine. The test car was driven over the 1975 Federal Test Procedure used in the U.S.A. for evaluation of automobile exhaust emissions, and the test engine was used to determine the catalysts conversion efficiency at 3600 r.p.m. Both sets of results show similar trends when expressed as percentage residual hydrocarbon emission (Fig. 2). All results show an increasing loss in performance as the running temperature increases; however, under similar operating temperatures the remote catalyst, 3, shows worse performance. The relative effects of

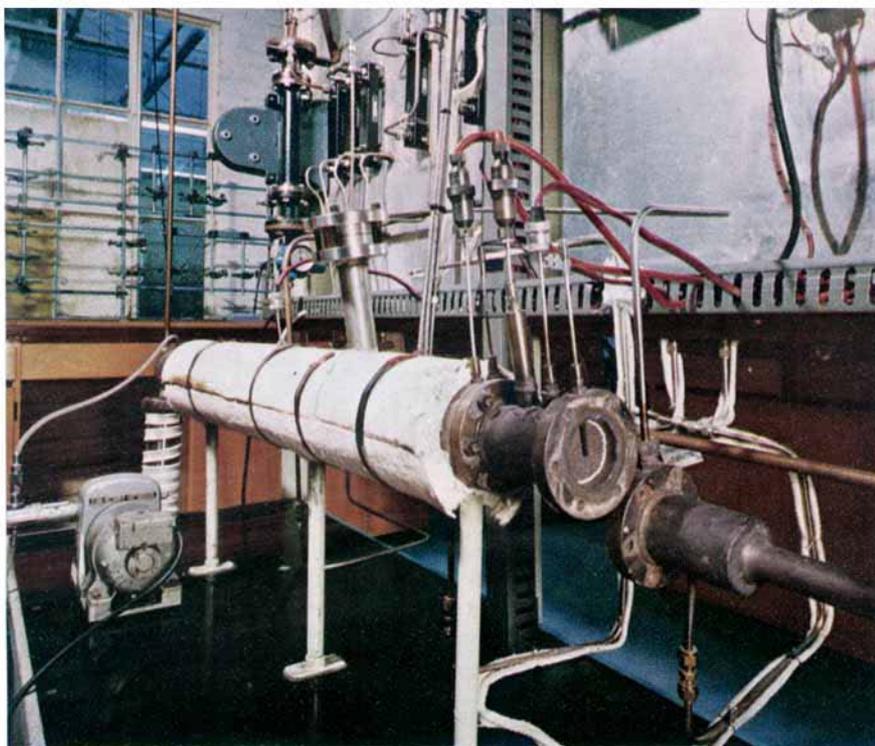
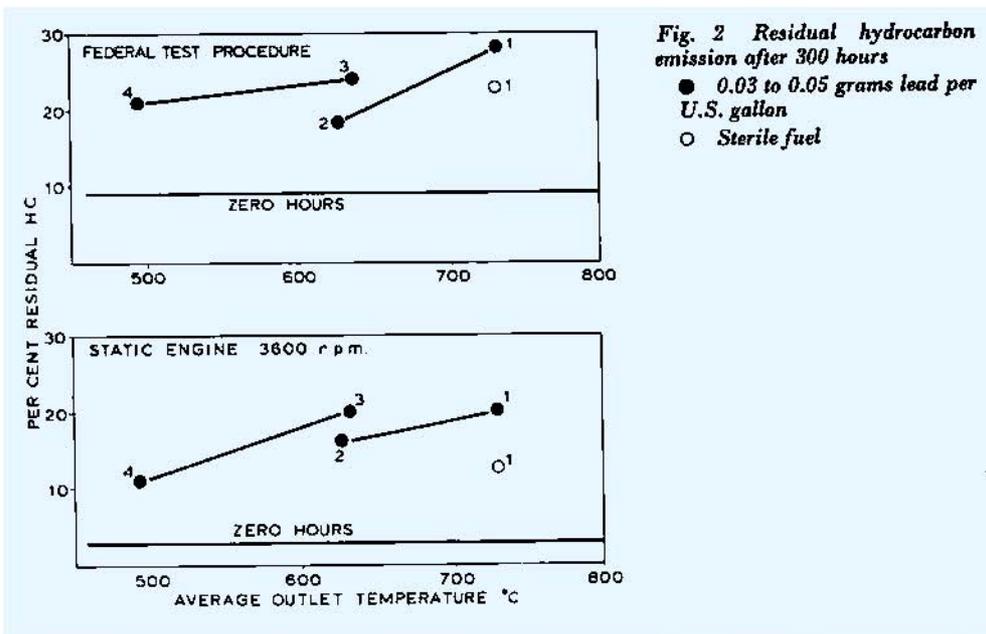


Fig. 3 The laboratory reactor system used as an exhaust gas simulator in investigating the poisonous characteristics of oxidation catalysts

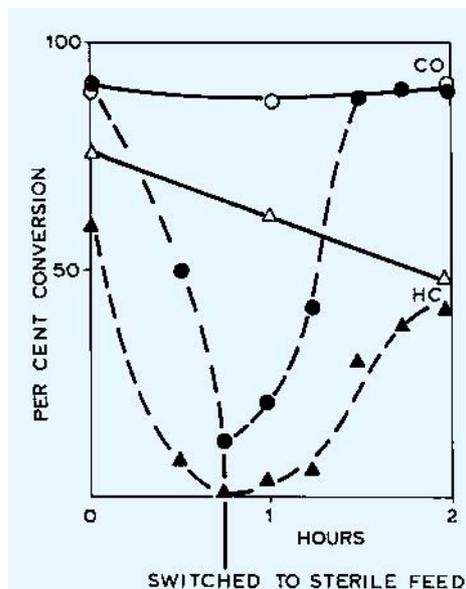


Fig. 4 Simulated poisoning of platinum CO/HC oxidation catalyst

○ △ Fresh catalyst
 ● ▲ Thermally aged catalyst
 Lead — 1.5 grams per U.S. gallon with stoichiometric ethylene dibromide

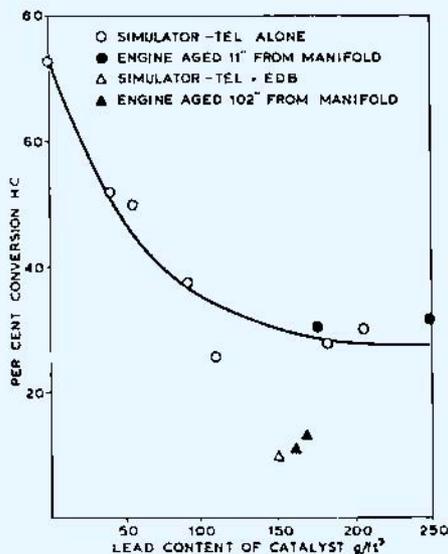


Fig. 6 Comparison of simulated and engine aged catalysts

TEL tetra-ethyl lead
 EDB ethylene dibromide

lead and sintering can be seen from the repeat test in position 1 using lead free fuel.

The basic reason for the pattern of results observed has been explored using an exhaust gas simulator (Fig. 3), in which the poisoning

was greatly accelerated by exposing the catalyst to a feed containing the equivalent of 1.5g Pb/U.S. gallon. The effect of thermal ageing on lead poison resistance is shown in Figure 4, and demonstrates the faster

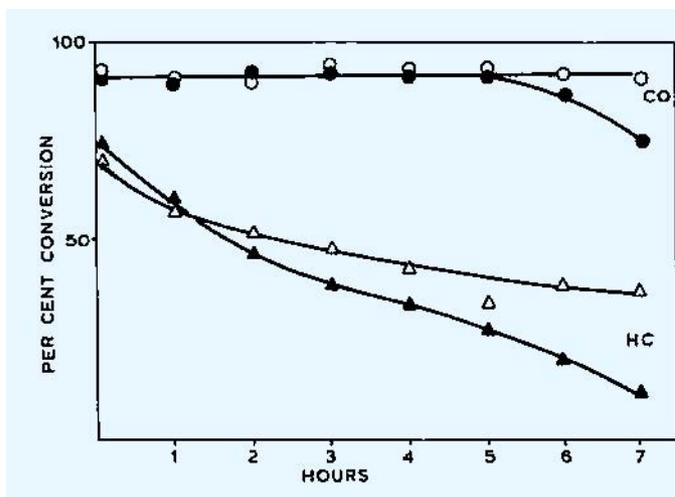


Fig. 5 Simulated poisoning of fresh catalyst

○ △ Lead — 1.5 grams per U.S. gallon
 ● ▲ Lead — 1.5 grams per U.S. gallon with stoichiometric ethylene dibromide

poisoning of the sintered catalyst. The poisoning process is also accelerated by the presence of halide scavenger, as shown in Figure 5. The greater toxicity in the presence of scavenger is reflected by the lower performance, even though the amount of lead deposited on the catalyst is reduced by the scavenging action.

Comparison of the performance of the engine aged catalyst and the simulator results shows good agreement for the samples run at similar operating temperature ($\sim 600^{\circ}\text{C}$) (Fig. 6). Further, the simulator has enabled us to deduce that the superior performance of the catalysts run in position 2 close to the manifold is due to the deposition of the less toxic lead oxide in this position, whereas in the remote position the more toxic lead halides and lead oxyhalides are deposited leading to greater catalyst degradation.

The good performance in position 2 was achieved even though the amount of lead deposited was the highest observed and approached nearly half the ingoing lead to the engine. Thus by judicious selection of the catalyst position and operating temperature catalyst deterioration can be minimised, the

catalyst is highly lead poison resistant, and can also act as an effective lead filter.

Design studies such as these have enabled Johnson Matthey to achieve emission levels below the United States Statutory Standards recommended for 1982 for over 50,000 miles vehicle operation.

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Palladium Flakes for Hydrogen Solid Storage Applications

Hydrogen appears capable of playing an important role in the provision of energy for the future. Whether it will provide all the answers to the world's fuel problems, as some believe, is open to discussion but it is certainly unlikely that it will quickly realise its full potential unless the problems which its exploitation will produce are anticipated and solutions to these problems found. Forward looking organisations throughout the world are now investigating many different aspects of hydrogen energy. A recent article by R. M. German and V. Ham, of the Sandia Laboratories, Livermore, California (*Internat. J. Powder Metall. Powder Technol.*, 1975, **11**, (2), 97-100) outlines and discusses a technique for the production of submicron thick metal flakes which appear potentially attrac-

tive for hydrogen solid storage applications.

On account of their hydride properties palladium and erbium were selected for investigation. In the case of the palladium, where pure sponge was the starting material, the process was carried out in ethyl alcohol using argon as a cover gas in an attrition mill containing 0.6 cm diameter hardened steel balls and running at a reduced speed of 60 r.p.m., which was found to minimise the disintegration of the flakes. Palladium has the advantage of flaking more readily than erbium and giving a considerably higher aspect ratio. Flakes having short diffusion paths, but without the handling properties generally associated with ultrafine powders, produced by this process have now been provided for hydrogen solid storage studies.