# Durability of Platinum-Containing Automotive Exhaust Control Catalysts

## IMPROVEMENTS IN RESISTANCE TO THERMAL DEGRADATION

### By B. J. Cooper

Johnson Matthey Inc., Catalytic Systems Division, Wayne, Pennsylvania

*Since the introduction in 1974 of catalytic converters for automotive emission control in the United States significant advances have been made in the design of durable monolith supported catalysts for the control of carbon monoxide, unburnt hydrocarbon and nitrogen oxide emissions. However, high temperature durability, has been a significant problem, particularly of three-way catalysts. Johnson Matthey Inc. have examined the fundamental nature of catalyst deactivation under high temperature conditions. This has been found to be associated with problems as diverse as adhesion of the catalyst layer to the ceramic monolith, interaction of the platinum metals with the underlying support and poor thermal stability of base metal promoters incorporated in the catalyst. As a result a new generation of catalysts has now been developed with substantially improved thermal stability.*

The use of catalyst systems for automotive emission control has provided a unique challenge to catalyst science since its introduction in the United States in 1974. The catalyst system is subjected to wide ranges of exhaust composition, temperatures that vary greatly and a considerable variety of catalyst poisons. As a result a number of control techniques have been designed to select the exhaust environment under which the catalyst works to maximum effect. The advent of the "three-way" catalyst to remove hydrocarbon, carbon monoxide and nitrogen oxide emissions simultaneously (1) requires close control of the air/fuel ratio (A/F) using an oxygen sensor feedback system, and has particularly accentuated the diversity of emission control systems.

European manufacturers favour oxygen sensor feedback electronic fuel injection systems, coupled with a single bed three-way catalyst. Japanese manufacturers favour feedback carburettors, coupled with either single bed three-way or single bed oxidation catalysts.

In the latter case, control of nitrogen oxides is obtained by the use of exhaust gas recirculation tolerant lean burn engines (2). In the United States the larger displacement engine families generally utilise a dual bed concept, with a three-way catalyst for hydrocarbon, carbon monoxide and nitrogen oxide control which is followed by an oxidation catalyst for residual clean up of any remaining hydrocarbons and carbon monoxide.

The dual bed system design has been successfully employed with both closed loop carburettors (A/F controlled via feedback from an oxygen sensor) and open loop (no oxygen sensor) systems. However, the use of such systems necessitates that the catalyst is effective over a wider range of air/fuel ratios, and more particularly that the catalyst is resistant to degradation over a wide range of temperatures during use.

The progressive decline of lead levels in so-called "unleaded gasoline" since its introduction in 1974 in the United States has reduced
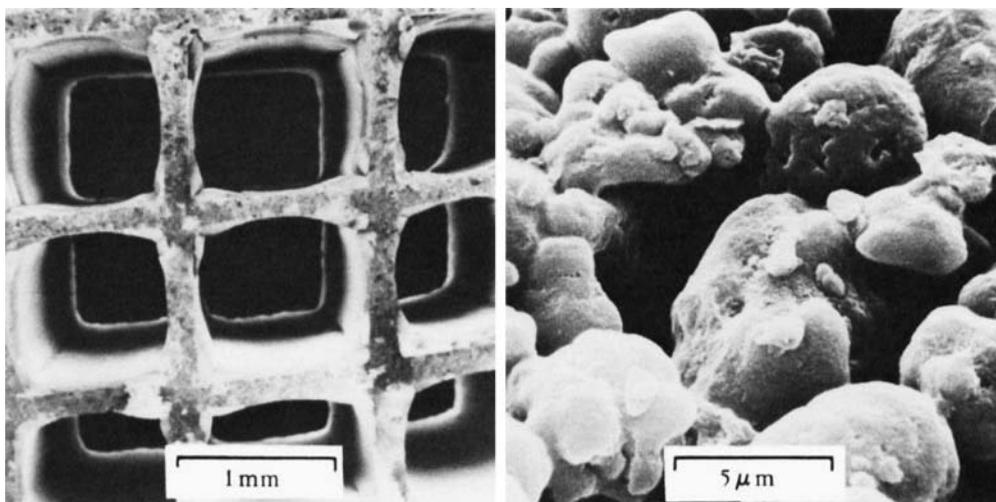
Fig. 1 Scanning electron micrographs of a washcoated ceramic monolith substrate showing, on the left, the open channel structure of the monolith with the washcoat layer deposited on the channel walls, and, right, at a higher magnification the porous structure of the washcoat

the problem of automotive catalyst poisoning. In examining the causes of automotive exhaust catalyst degradation during many thousands of hours of catalyst testing the conclusion is reached that thermal degradation is the major cause of loss of catalyst performance. This may be demonstrated by comparing the performance of a three-way catalyst subjected to short thermal abuse, with that of a catalyst that has

run for hundreds of hours on an engine dynamometer (Table 1).

Comparison of the catalyst which had reached 870°C (for 8 per cent of the ageing period) with the catalyst aged at 700°C (8 per cent of the ageing period) shows that the higher ageing temperature had significantly lowered the activity of the catalyst for carbon monoxide and nitrogen oxide control. Furthermore, a

**Table I**

**Comparison of 12:1 Platinum:Rhodium Three-Way Catalyst Performance after Ageing on an Engine Using 10 mg/Pb/U.S. gallon, with that of a High Temperature Furnace Aged Catalyst, Conversions Were Measured in Perturbating Exhaust ± 1A/F, 1 hertz**

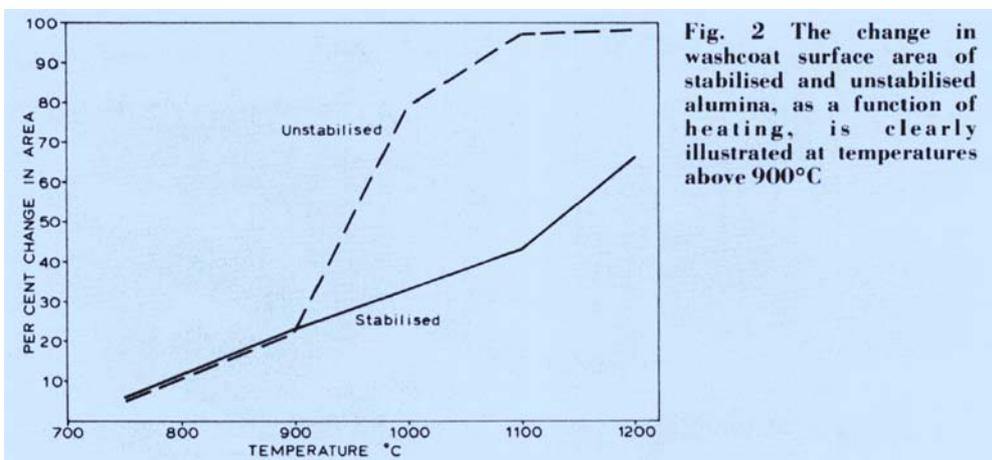| Catalyst ageing | Per cent conversion at stoichiometric air/fuel ratio | | |
|---|---|---|---|
| | Hydrocarbons | Carbon monoxide | Nitrogen oxides |
| 300 hours engine ageing at maximum temperature 700°C | 94 | 92 | 92 |
| 300 hours engine ageing at maximum temperature 870°C | 90 | 70 | 69 |
| 1 hour furnace ageing at 980°C in air | 90 | 53 | 60 |

Fig. 2 The change in washcoat surface area of stabilised and unstabilised alumina, as a function of heating, is clearly illustrated at temperatures above 900°C

short furnace ageing for 1 hour at 980°C had an even more severe effect on the performance of the catalyst system. As a result of these observations, Johnson Matthey concentrated upon improving the resistance of their automotive catalysts against thermal degradation.

## Washcoat Stabilisation

Johnson Matthey automotive emission control catalysts consist of a high surface area alumina support or "washcoat" containing platinum metals, coated on either a ceramic monolith substrate (1,3), or metal monolith substrate (4). Scanning electron micrographs of a typical cross section of a washcoated ceramic monolith catalyst and of the porous washcoat structure at higher magnification are shown in Figure 1.

The use of high surface area alumina supports to maximise the dispersion of noble metals is general practice in the manufacture of catalysts. However, in automotive applications it is essential that high surface areas are maintained in an exhaust environment where
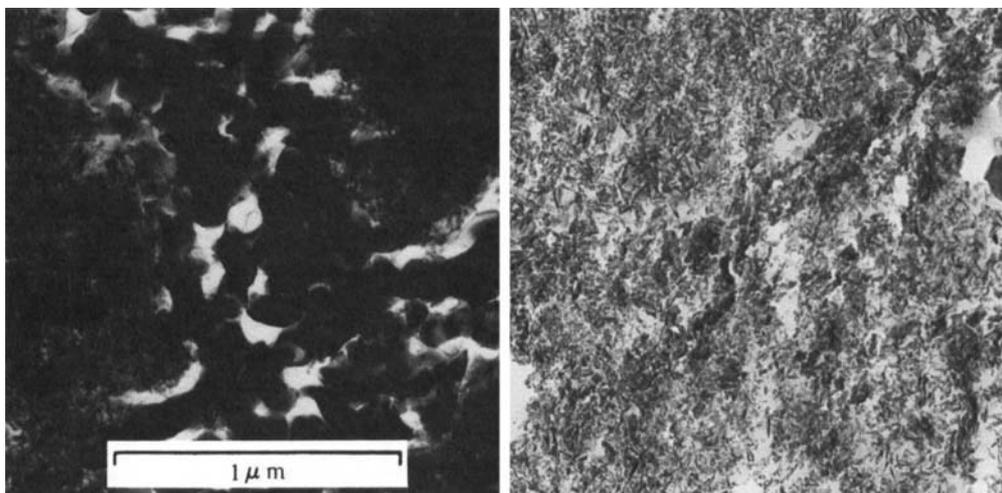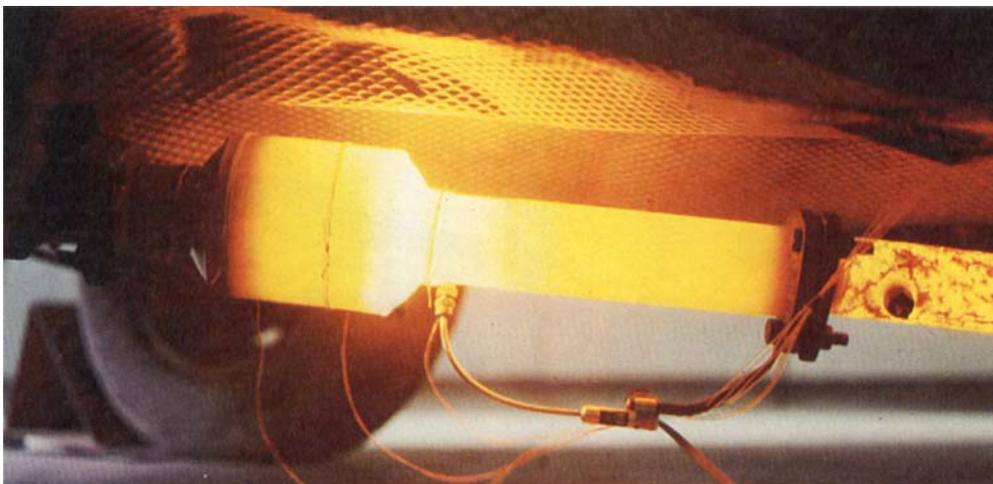


Fig. 3 Transmission electron micrographs of alumina washcoats heated to 1100°C in air showing, left, the presence of low surface area α-alumina in the unstabilised washcoat and, right, the absence of the α-alumina in the stabilised washcoat

Fig. 4 High temperature destructive testing of an automotive emission control catalyst simulating the conditions that could result from ignition malfunction. Intermittent misfire in the ignition system can increase the temperature of the catalyst to above 1100°C

temperatures may exceed 1000°C. As a result, it is common to incorporate alkali metal oxides, alkaline earth metal oxides or rare earth oxides as surface area stabilisers (5) (Figure 2). Use of such stabilisers can retard the phase change of alumina to the dense, low surface area α-alumina form up to temperatures of about 1100°C. Transmission electron micrographs clearly show the formation of low surface area α-alumina in unstabilised washcoat heated to 1100°C, and its complete absence in the stabilised washcoat treated at the same temperature, see Figure 3.

As a result of the use of surface area stabilisers, the operating capabilities of three-way and oxidation catalysts can be improved so that detrimental washcoat surface area loss is not encountered until about 1100°C. However, intermittent misfire in a vehicle ignition system can increase the catalyst temperature beyond 1100°C, see Figure 4. Under such conditions transformation to α-alumina can still occur and the result of this high temperature alumina transformation is extremely detrimental. Densification of the washcoat structure results in severe cracking of the washcoat with potential loss of the catalyst layer from the underlying substrate, Figure 5 (left). Clearly, it is necessary to prevent such loss of catalyst at

high temperatures. Modification of the alumina structures used in the washcoating process at Johnson Matthey has enabled significant retardation of the washcoat's tendency to densify at high temperature. Comparison of the two washcoat systems illustrated in Figure 5 shows that the severe cracking that occurs after heating to 1350°C can be essentially eliminated. Furthermore, tests of the new stabilised high temperature washcoat incorporated into a platinum/palladium oxidation catalyst revealed much reduced catalyst deterioration, Figure 6.

## Thermal Degradation of Three-Way Catalysts

The thermal deactivation of three-way catalysts which operate in a redox system oscillating between rich and lean air/fuel ratios is more complex. The deactivation process is dependent upon the chemical environment of the catalyst system. Furnace ageing of a platinum/rhodium three-way catalyst at 870°C, Figure 7, in atmospheres of nitrogen, hydrogen/nitrogen and air shows that oxidative ageing is the most detrimental. Thus air ageing results in a light off temperature for hydrocarbons, carbon monoxide and nitrogen oxides some 30 to 50°C higher than after reduction. This effect has been attributed to interaction of
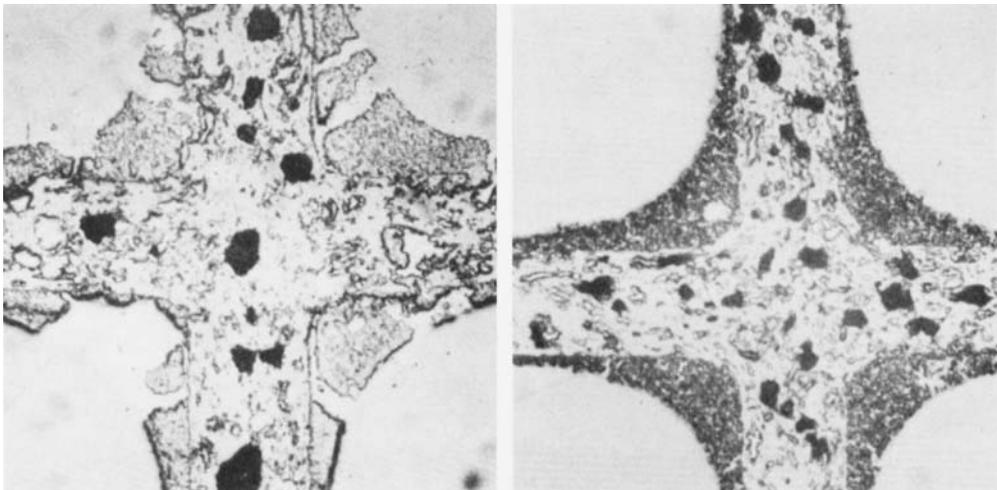
Fig. 5 Optical micrographs of a monolith cell wall and washcoat showing, left, loss of washcoat during severe high temperature treatment and, right, the retention of the high temperature stabilised coating after a similar treatment, at 1350°C ×95 approx.

rhodium oxide with $\gamma$-alumina in the washcoat (6), and is elegantly demonstrated by ageing a catalyst in the absence of an alumina washcoat, Figure 8. After ageing in air at 1200°C the standard $\gamma$-alumina containing three-way catalyst performs significantly better for carbon monoxide and hydrocarbon control in terms of lower light off temperature. However, nitrogen oxide control of the standard catalyst is, in fact, worse than the catalyst prepared via impregnation of platinum and rhodium onto an unwashcoated monolith substrate. Since nitrogen oxide control is principally due to the

rhodium content of the catalyst, it is therefore inferred that removal of $\gamma$-alumina from the catalyst eliminates the detrimental rhodium-gamma alumina interaction.

An alternate method of eliminating the interaction between rhodium and alumina is deliberately to support the rhodium on a different oxide. Work at Ford Motor Company (7) and Johnson Matthey (8) has shown that by supporting rhodium on zirconia the activity of the catalyst can be maintained after high temperature oxidative treatment, Figure 8. Tests of the rhodium/zirconia catalyst on an
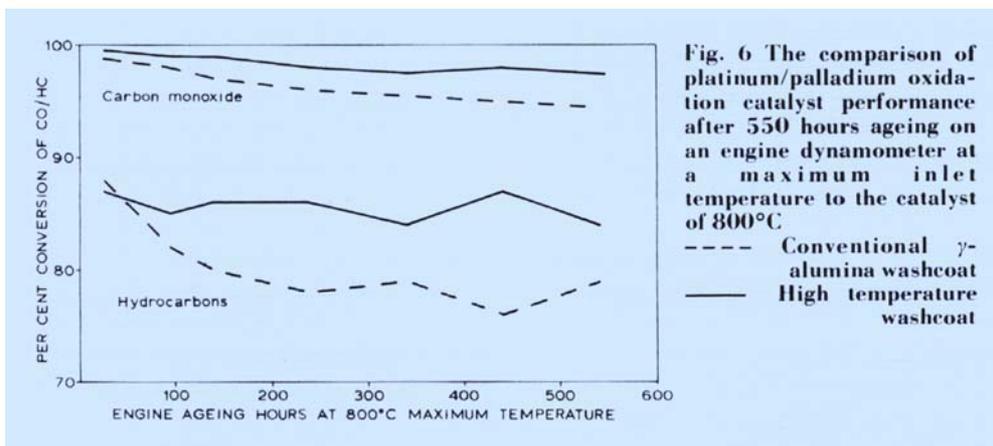


Fig. 6 The comparison of platinum/palladium oxidation catalyst performance after 550 hours ageing on an engine dynamometer at a maximum inlet temperature to the catalyst of 800°C
- - - -  Conventional $\gamma$-alumina washcoat
———  High temperature washcoat

**Fig. 7 The effect of ageing atmosphere on the light off temperature performance of a platinum/rhodium three-way catalyst, showing the detrimental effect of ageing in an oxidising environment**

Air

Hydrogen/Nitrogen

Nitrogen
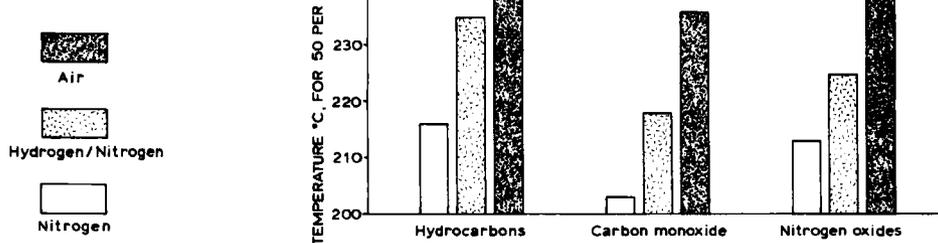
**Fig. 8 The effect of high temperature ageing in an oxidising environment of platinum/rhodium three-way catalysts showing the advantage of substitution of zirconia for alumina as a support for rhodium**

Rhodium/Zirconia washcoat

Standard three-way catalyst

No washcoat
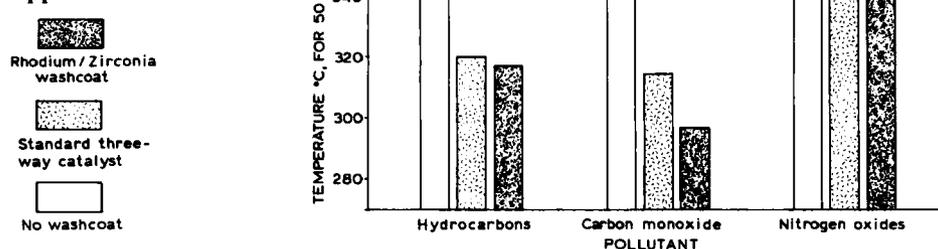
engine after treatment at 950°C in air show significant improvement in the control of hydrocarbon, carbon monoxide and nitrogen oxide emissions, Figure 9.

Unfortunately, the incorporation of rhodium/zirconia into three-way catalysts requires a complex manufacturing method which is not suitable for high speed production of many millions of automotive catalysts per year. Therefore, Johnson Matthey have explored alternate methods of modifying conventional $\gamma$-alumina washcoat to minimise rhodium-alumina interaction. Comparison of air/fuel ratio scans after the ageing at 950°C of a rhodium $\gamma$-alumina catalyst with a rhodium catalyst deposited on a modified alumina washcoat shows, in Figure 10, the significant improvement in nitrogen oxides control

obtained at air/fuel ratios rich of stoichiometry.

## Thermally Stable Single Bed Three-Way Catalysts

With progressive improvements in feedback carburettor technology improved air/fuel ratio control is being achieved. However, as demonstrated in Figure 10, the major problem to be overcome with three-way catalyst operation is thermal degradation of carbon monoxide control. Incorporation of base metal promoters into three-way catalysts such as nickel (9) and cerium (10) results in improved carbon monoxide control, Figure 11. From Figure 11 it is evident that the addition of base metal promoters has a strong influence on three-way catalyst performance. Utilisation of such effects to their maximum benefit is vital to the design
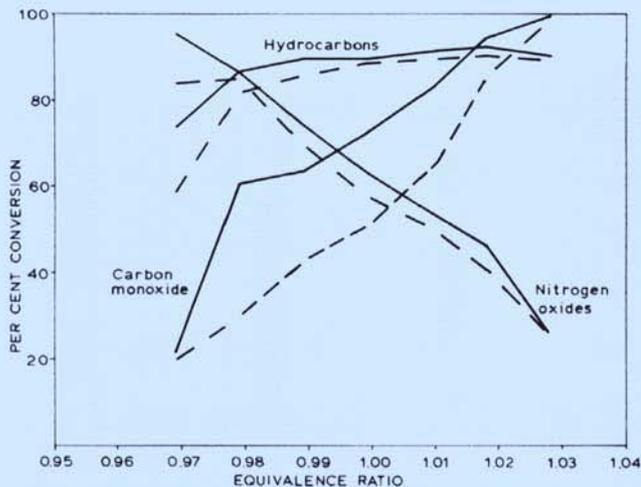
Fig. 9 Comparison of rhodium on alumina, and on zirconia after an oxidising treatment at 950°C. Performance is measured on an engine to determine conversion of the three pollutants as a function of equivalence ratio of the exhaust gas
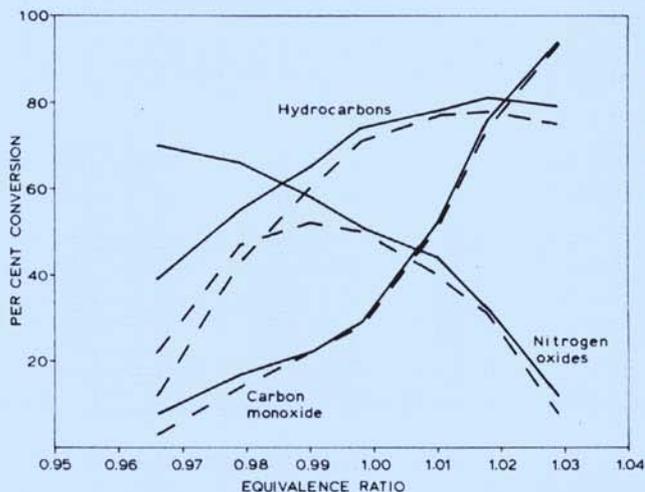——— Rhodium/zirconia
- - - - Rhodium/alumina

Fig. 10 Comparison of two rhodium catalysts after an oxidising treatment in air at 950°C for conversion of the three pollutants, as a function of equivalence ratio
- - - - Rhodium/$\gamma$-alumina
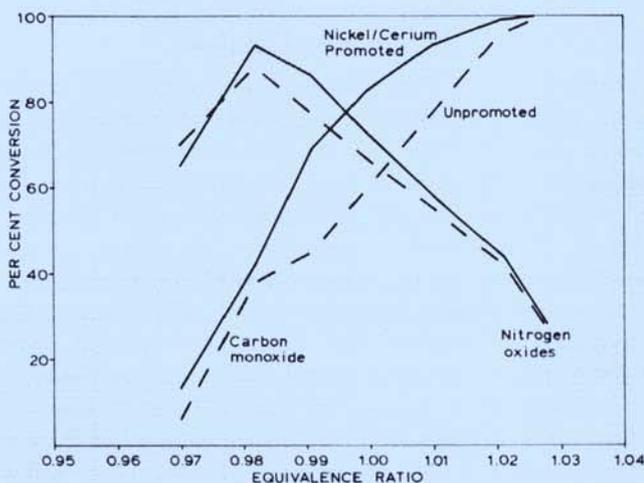——— Rhodium/modified alumina

Fig. 11 Comparison of nickel/cerium promoted, and also unpromoted platinum/rhodium three-way catalysts for the conversion of carbon monoxide and nitrogen oxides, as a function of exhaust gas equivalence ratio
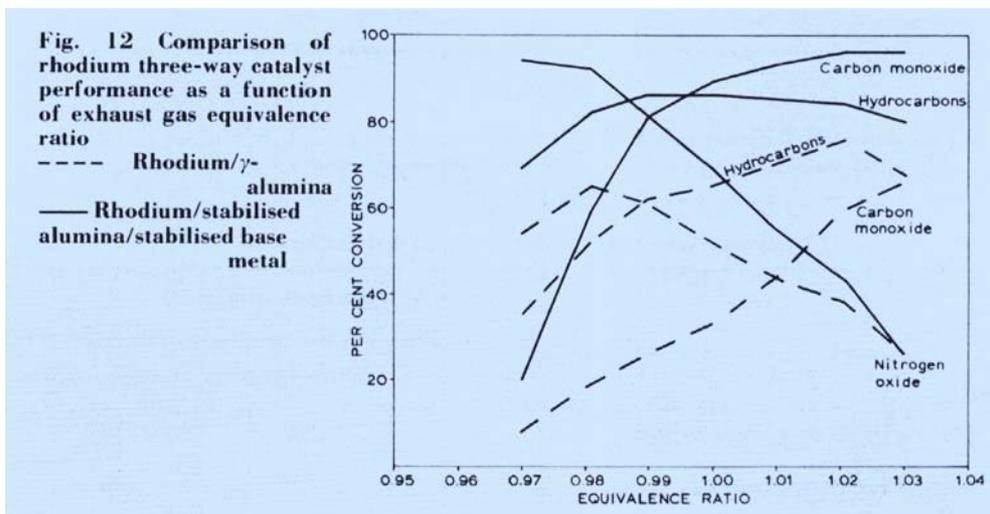
of high performance three-way catalyst systems. The promotion of three-way catalysts by the incorporation of a thermally stable base metal promoter was therefore selected as a catalyst design objective. Furthermore, it was considered essential that the promoter system should have no detrimental effect on the small amount of rhodium contained in the three-way catalyst. Study of a variety of base metal promoter systems utilising a test sequence where the catalyst is aged for 25 hours on an engine dynamometer and then subjected to thermal degradation at 980°C in 2 per cent oxygen/10 per cent water has led to a new catalyst system that is much more thermally stable. Comparison of two rhodium catalysts after thermal treatment, Figure 12, shows the massive improvement obtained in hydrocarbon, carbon monoxide and nitrogen oxide control with the new catalyst.

## Durability of Thermally Stable Three-Way Catalysts

From the discussions above it can be seen that the thermal stability of three-way catalyst systems can be improved by (a) modification of the washcoat system to eliminate loss of washcoat under very high temperature operation, (b) stabilisation of the washcoat to minimise rhodium/$\gamma$-alumina interaction and (c)

promotion of the activity of rhodium by the incorporation of thermally stable base metal additives. In addition, careful optimisation of the base metal additive in combination with the platinum metals in the catalyst can lead to the best possible use of the noble metals in the converter. For example, durability tests of three different catalysts containing from 0.0750 to 0.0475 troy ounces of noble metals reveal that superior catalytic performance can be obtained by the correct combination of the washcoat, base metals and platinum metals. The data shown in Table II were obtained after 300 hours ageing on an engine durability cycle at 790°C maximum operating temperature for 11 per cent of the ageing period. From Table II it is evident that a significant improvement in carbon monoxide control is obtained using the thermally stabilised base metal promoter (catalyst B) in place of the conventional nickel/cerium three-way catalyst (catalyst A) in a platinum/palladium/rhodium catalyst. In addition, use of the thermally stabilised washcoat and base metal promoter in combination with the optimum platinum and rhodium content in the catalyst results in further improvement in performance (catalyst C).

Finally the technology described above has been evaluated by testing three-way catalytic converters in the U.S. Federal Test Procedure



Fig. 12 Comparison of rhodium three-way catalyst performance as a function of exhaust gas equivalence ratio

- - - - Rhodium/$\gamma$-alumina

——— Rhodium/stabilised alumina/stabilised base metal

after ageing the converters for 300 hours at a maximum temperature in the range of 750 to 800°C for 50 per cent of the ageing period. The results in Table III indicate the improved conversion levels for hydrocarbons, carbon monoxide and nitrogen oxides obtained with the thermally stable catalyst in comparison with a conventional nickel/cerium three-way catalyst.

## Catalyst Development for Future Engine Systems

Earlier work on catalytic converters first concentrated on improvements in resistance to poisoning (11,12) and has now resulted in improvements in thermal stability. The catalytic converters of the future will have to meet additional stringent performance requirements to meet emission levels on the new generation of fast burn-low friction engines now emerging. These engines typically run with much cooler exhaust gas temperatures necessitating good low temperature performance. In addition, new problems are emerging related to the mechanisms of catalyst degradation at low temperature (13). New challenges still lie ahead for the catalyst scientist, and Johnson Matthey is continuing its efforts in these new areas.

**Table II**

**Conversion Efficiency of Catalytic Converters at Stoichiometric Air/Fuel Ratio after 300 hours Engine Ageing at 790°C Maximum Temperature**

| Catalyst | Noble metal content troy ounces/converter | | | Per cent conversion | | |
|---|---|---|---|---|---|---|
| | Platinum | Palladium | Rhodium | Hydro-carbons | Carbon monoxide | Nitrogen oxides |
| A Conventional nickel/cerium | 0.05 | 0.02 | 0.005 | 89 | 73 | 72 |
| B Thermally stabilised promoter | 0.05 | 0.02 | 0.005 | 90 | 82 | 72 |
| C Thermally stabilised washcoat and promoter | 0.04 | — | 0.0075 | 91 | 85 | 77 |

**Table III**

**Conversion Efficiency of Catalytic Converters during the U.S. Federal Test Procedure after Engine Ageing for 300 hours at 750-810°C Maximum Temperature**

0.048 Platinum and 0.0095 Rhodium troy ounces/Converter

| | Per cent conversion | | |
|---|---|---|---|
| | Hydrocarbons | Carbon monoxide | Nitrogen oxides |
| Conversion nickel/cerium three-way catalyst | 82 | 53 | 72 |
| Thermally stabilised three-way catalyst | 90 | 71 | 79 |

# References

1 B. Harrison, B. J. Cooper and A. J. J. Wilkins, *Platinum Metals Rev.*, 1981, **25**, (1), 14

2 H. Kuroda, Y. Nakajima, K. Sugihara, Y. Takagi and S. Muranaka, S.A.E. Paper No. 780006, 1978

3 G. J. K. Acres and B. J. Cooper, *Platinum Metals Rev.*, 1972, **16**, (3), 74

4 C. A. Dulieu, W. D. J. Evans, R. J. Larbey, A. M. Verrall and A. J. J. Wilkins, S.A.E. Paper No. 770299, 1977

5 R. Gaugin, M. Graulier and D. Papee, Adv. in Chem. Series 143, ed. J. E. McEvoy, A.C.S., Washington, D.C., 1975

6 H. C. Yao, H. K. Stepien and H. S. Gandhi, *J. Catal.*, 1980, **61**, (2), 547

7 H. K. Stepien, W. B. Williamson and H. S. Gandhi, S.A.E. Paper No. 800843, 1980

8 J. V. Minkiewicz, B. J. Cooper and M. R. Baxter, A.I.Ch.E. Summer National Meeting, Detroit, August 1981

9 B. J. Cooper and L. Keck, S.A.E. Paper No. 800461, 1980

10 G. Kim, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**, (2), 267

11 B. J. Cooper, *Platinum Metals Rev.*, 1975, **19**, (4), 141

12 A. F. Diwell and B. Harrison, *Platinum Metals Rev.*, 1981, **25**, (3), 142

13 H. S. Gandhi, W. B. Williamson and J. L. Bomback, *Appl. Catal.*, 1982, **3**, (1), 79

# New Location for Platinum Facility

The Johnson Matthey Group has recently relocated its Belgian operations in the Evere-Brussels industrial estate. The new factory provides a wide range of facilities for the production and fabrication of platinum and the other noble metals, particularly for industry but also for dental and jewellery applications.

Many of the activities are very specialised. In the weaving shop illustrated here four looms are used for weaving catalyst gauzes in plain and herringbone patterns from 60 to 100 microns diameter wire. Employing one of the largest looms of its type in the world SA Johnson Matthey NV can weave gauzes up to five metres in width. Rolling mills located in a dust-free area are dedicated to the platinum metals, thus avoiding the possibility of contaminating the products, which include bushings and spinner baskets for the fibre glass industry, and laboratory apparatus.

Now located near to both the international airport and the motorway that surrounds Brussels, the size and organisation of the company ensures a flexibility that enables it to respond rapidly to the needs of its national and international customers.