

Advances and Developments in Emissions Control

A REVIEW OF THE 1992 SAE INTERNATIONAL CONGRESS

The Society of Automotive Engineers International Congress, held in Detroit, Michigan, U.S.A. from 24th to 27th February 1992, continues to be the worldwide forum for the presentation and discussion of matters relating to vehicle emissions control. Despite the recession the sessions were very well attended, and papers were presented by speakers from around the globe.

Broadly speaking, the contributions can be divided into two main categories, gasoline- and diesel-related. A recurrent theme throughout was the emphasis upon the fact that noble metal catalysts, particularly in gasoline applications, are very much part of a control system involving engine management strategies and other engine components.

Catalyst Design for Diesel Applications

Noble metal catalysts for use on diesel engines were the subject of several papers, with interest in the U.S.A. focused on heavy duty engine applications.

The optimisation of noble metal formulations for diesel catalysts which could exhibit good control of the volatile organic fraction of the particulate matter, and also limit the formation of sulphates which can otherwise increase particulate emissions was reviewed by M. G. Henk, W. B. Williamson and R. G. Silver of Allied Signal Inc. (SAE 920368). Platinum, palladium and rhodium can all cause the formation of sulphate but it was demonstrated that palladium systems can be optimised to limit this undesirable effect.

The role of a noble metal flow-through oxidation catalyst as part of a strategy for the development of a low emissions specification heavy duty engine was considered by F. Brear of Perkins Technology Ltd., and S. Fredholm and

E. Anderson of Svenska Emissionsteknik AB (SAE 920367). The problem of sulphate generation over noble metal catalysts was again highlighted. The authors conclude that while it is possible to modify the platinum content and thus its interaction with other catalyst components, in order to reduce sulphate emissions, the solution may have to include a substantial reduction in the sulphur content of diesel fuel. This conclusion was reinforced in a paper by R. J. Farrauto and J. J. Mooney of Engelhard Corporation (SAE 920557).

Autocatalyst Systems

Two papers in particular provoked excitement and debate. Both considered the application of noble metal autocatalysts as part of advanced development systems designed to speed-up activation of the catalyst when cold. It is generally recognised that the major portion of both hydrocarbon and carbon monoxide emissions are produced within the first two minutes of the vehicle drive cycle, that is while the catalyst is cold. One potential control strategy involves the use of electrically heated catalysts and these have been the subject of papers at previous Congresses.

A more radical approach to the cold-start emissions problem was described by T. Ma of Ford Motor Co., N. Collings of Cambridge University and T. Hands of Combustion Ltd., (SAE 920400). Substantial reductions in cold-start emissions have been demonstrated by a strategy which causes the engine to run rich, together with air-injection and the use of electrodes – positioned in front of the conventional noble metal catalyst – for the first few seconds of vehicle operation.

L. S. Soucha, Jr. and D. F. Thompson of Corning Inc., detailed their investigations (SAE 920093). They concluded that future

emissions standards legislation could be achieved with an electrically heated platinum-rhodium-containing converter, using an extruded metal substrate in conjunction with a conventional noble metal catalyst.

A paper by W. A. Whittenberger and D. T. Sheller of Camet Co., and J. Walters of Gordon-Darby Inc., gave experiences of user vehicles equipped with electrical heated catalysts (SAE 920722). It indicated a number of areas where improved technology might make such equipment more viable; these included battery and power control technologies.

Catalyst Design for Gasoline Vehicles

It was reported by J. C. Dettling and Y. K. Lui of Engelhard Corporation that platinum-palladium catalysts could be made to perform more like rhodium-containing catalysts for the control of oxides of nitrogen, than had previously been shown (SAE 920094). The platinum-palladium systems described are 85 per cent as effective as a platinum-rhodium system for the control of nitrogen oxides emissions on a vehicle, at reduced overall noble metal loadings. The authors conclude that it may be possible to meet forthcoming emission standards without increasing the usage of rhodium per vehicle.

The utilisation of palladium, this time as a substitute for platinum, was reviewed by C. N. Montreuil, S. C. Williams and A. A. Adamczyk of Ford Motor Co., as part of a programme to generate an experimental data base of catalyst conversion efficiency (SAE 920096). Platinum-rhodium and palladium-rhodium catalysts at equivalent concentrations and ratios were examined in a tubular flow reactor. Steady state conversion efficiencies for carbon monoxide, nitric oxide, propane, propylene, hydrogen and oxygen through the catalysts were determined for a variety of inlet species, concentrations and inlet gas temperatures. The results of these experiments show significant improvements in carbon monoxide and nitric oxide conversion efficiencies for both of these catalyst systems compared with previous generation catalyst formulations, when the feed-gas stoichiometric

ratio was on the rich side. The conversion efficiencies obtained with the platinum-rhodium formulation were similar to those obtained with the palladium-rhodium formulation over a wide range of conditions. Differences were noted, however, at low temperatures or when a high concentration of "slow" burning hydrocarbons (propane) was present.

The subject of noble metal cost optimisation was addressed by M. A. Härkönen and P. Talvitie of Kemira Oy (SAE 920395). Various dual bed catalysts containing different platinum-rhodium, palladium-rhodium, platinum and palladium loadings, and combinations thereof, were subjected to oven and bench engine ageing techniques, and then examined for performance. It was found that catalyst performance is not necessarily proportional to the cost of the noble metals used, and that although palladium and palladium-rhodium catalysts have good thermal ageing resistance they are more sensitive to the presence of poisons than either platinum or platinum-rhodium. Also, the addition of ceria to a three-way catalyst is more beneficial for platinum-rhodium, platinum and rhodium systems than for palladium-rhodium catalysts.

A prominent topic emerging from the papers dealing with three-way catalysts was catalyst deactivation modes, and their effects on emissions. A number of these papers dealt with thermal deactivation and the role of air to fuel ratio.

A paper by N. A. Hannington, R. J. Brisley and R. D. O'Sullivan of Johnson Matthey described the effects of catalyst ageing under different temperature and air to fuel ratio conditions, and compared the emissions of these catalysts to those from catalysts aged on vehicles driven under European conditions (SAE 920399). It was concluded that bench engine ageing which gave catalyst inlet temperatures in excess of 850°C, with significant amounts of lean running, most closely simulated "real life" European ageing on vehicles and that these high temperature, lean ageing conditions resulted in greater deterioration of platinum-rhodium catalysts.

Information on the effect of oxygen concentration on the ageing of three-way catalysts using inlet temperatures in excess of 850°C was presented by R. M. Heck, J. K. Hochmuth and J.C. Dettling of Engelhard Corporation (SAE 920098). Higher catalyst temperatures are seen as the converter is moved closer to the engine to reduce cold start emissions. This, in combination with lean conditions resulting from a fuel cut-off strategy on deceleration, may give the high temperature, lean conditions described in the paper. It was found that catalyst deactivation increased with higher temperatures and with increasing oxygen concentration.

High catalyst temperatures leading to deactivation may also be experienced during ignition-induced misfire. This topic was described by C. D. Tyree of the U.S. Environmental Protection Agency (SAE 920298). Vehicles were run over the Federal Test Procedure cycle with varying degrees of ignition-induced misfire. It was found that hydrocarbon emissions were increased the most by this type of misfire, whereas much higher misfire rates were required to increase carbon monoxide tailpipe levels to the same extent. Nitrogen oxides emissions were reduced as the rate of misfire increased. Catalyst temperatures could be increased by up to 300°C while driving over the Highway Cycle with 20 per cent misfire, although during the Federal Test Procedure cycle, with the equivalent of one cylinder of a six cylinder engine permanently misfiring, the catalyst temperature reached an average of 600°C and a maximum of 851°C.

Catalysts may also become deactivated by poisons contained in both fuel and lubricating oil. The effect of oil-derived phosphorus and sulphated ash on catalyst deactivation was described by K. Inoue, T. Kurahashi and T. Negishi of Nippon Oil Company and K. Akiyama, K. Arimura and K. Tasaka of Toyota Motor Corporation (SAE 920654). They found that the catalyst surface phosphorus concentration increased with increasing carbon monoxide and nitrogen oxides emissions. The presence of sulphated ash reduced the amount

of phosphorus on the catalyst but also had a negative effect on catalytic activity. Catalyst deactivation was also much more apparent at 800°C than at 720°C. They concluded that engine oils low in phosphorus and sulphated ash can reduce catalyst deactivation.

The effect of fuel sulphur and air to fuel ratio on catalyst deactivation was described by J. C. Summers, J. F. Skowran, W. B. Williamson and K. I. Mitchell of Allied Signal Inc., (SAE 920558). It was reported that relatively low concentrations of fuel sulphur resulted in loss of catalyst performance, but little additional poisoning effect is seen on increasing the sulphur content of the fuel to comparatively high levels. This deterioration in emissions is due to the diminished performance of a catalyst at its operating temperature, rather than to an increase in light-off temperature.

Catalyst selection for the reduction of formaldehyde emissions from methanol-fuelled vehicles was presented by M. S. Newkirk and L. R. Smith from Southwest Research Institute, M. Ahuja, S. Albu and S. Santoro from California Air Resources Board, and J. Leonard from South Coast Air Quality Management District (SAE 920092). The use of methanol as a fuel is seen as a viable approach to reduce air pollution; concern, however, has been expressed about the relatively high formaldehyde emissions from vehicles using this fuel. This paper reported on investigations during which the catalyst systems of several vehicles were modified in order to reduce formaldehyde emissions. In general the strategy was to reduce cold start emissions by using close coupled and electrically heated catalyst systems. These techniques were successful, but supplemental air injection above the catalyst was required when using an electrically heated catalyst to optimise this system.

Conclusions

The Society of Automotive Engineers Congress is always a barometer to the current areas of work and interest of the car companies and of the emissions control industry. The need to meet forthcoming emissions legislation clearly

drives development activities. This was highlighted by the papers which considered improved cold-start performance and in the attention given to catalyst deactivation mechanisms, by temperature and/or poisoning.

The application of noble metal catalysts for diesel emissions control continues to be a major part of the Congress, as are papers considering the substitution of platinum or rhodium by palladium. C.J., R.D.O'S.

Platinum Group Metals in 1991

The Ayrton Metals Platinum Yearbook 1992

BY B. H. NATHAN, Woodhead Publishing, Cambridge, 1992, 195 pages, ISBN 1-85573-084-7, £45.00

Following in the footsteps of the "Platinum Yearbook 1991", this new publication sets out to present a panorama of the many events that influenced the market for platinum group metals during 1991. These are covered in general terms, and in considerable detail in Chapters 1 and 2, respectively, both being supported by statistical data. A number of these events were industrial announcements or scientific reports, but most were not, and the whole makes fascinating reading, perhaps especially for those whose involvement with the platinum group metals does not embrace metal dealing.

While the detailed review of 1991 occupies ninety-nine pages, the prospects for the six platinum group metals in 1992 are contained in some five pages. It is suggested that of these metals, "platinum has the best prospects for a sound and widely-based recovery in 1992".

A chapter on the Tokyo Commodity Exchange by Kazuhiko Noma is complemented by two further chapters by Brian Nathan, in which the dealing arrangements for the London Platinum and Palladium Market and the New York Mercantile Exchange are considered.

An interesting overview of fuel cells and their state of development for stationary and transportation applications is given by Jocelyn Cloete. Once again, it is concluded that proof of phosphoric acid fuel cell technology will be provided in the imminent future, from the results of on-going field tests.

In the penultimate chapter Peter Gaylard outlines the lengthy, complex and expensive processes that are necessary to extract the platinum group metals from the limited number of major ore bodies in which they occur, in minute quantities, and to then refine them to the required high purity levels. In response to the needs of the market, and to a greater awareness of environmental considerations, improved recovery processes have been introduced in recent years.

A brief chapter on the history of platinum and the platinum group metals, based in part upon "A History of Platinum and its Allied Metals" by D. McDonald and L. B. Hunt, concludes this informative and interesting book which will serve as more than a record of the events of the past year. I.E.C.

Platinum Improves Protective Coatings

Gas turbine engines are widely used for both stationary and mobile applications, and the turbine blades, which are highly stressed during service, are required to operate at high temperatures in oxidising atmospheres which may be contaminated with corrosive fuel residues and ingested salts. To some extent nickel-based superalloy turbine components can be protected against both oxidation and hot corrosion by nickel aluminide diffusion coatings, but in more severe environments the protective coating may break down, reducing service life.

The development of platinum-containing coating systems has been reported here on several occasions over the past decade as materials

scientists have sought both to improve the protection given by such coatings and to establish the precise role of the platinum in the process.

A further contribution on the subject has been published recently (H. M. Tawancy, N. M. Abbas and T. N. Rhys-Jones, *Surf. Coat. Technol.*, 1991, 49, (1-3), 1-7).

Following an investigation of the microstructure of platinum-modified aluminide coatings on selected nickel-based superalloys, the authors identify a number of ways by which the platinum improves the protective ability of the coating. Oxidation behaviour depends upon the composition of the superalloy substrate, especially on its rare earth content.