

Controlling Automobile Emissions

Attendance at the 1991 Society of Automotive Engineers International Congress and Exposition held in Detroit, Michigan, U.S.A. from 25th February to 1st March, 1991, was affected by the conflict in the Middle East; in particular representation from Europe and Japan was considerably less than usual. Nevertheless there was an extensive programme of technical papers covering many aspects of the motor car in a number of parallel sessions, several of which covered emissions technology.

A new impetus to developments in autocatalyst technology has resulted from the recently announced Clean Air Act in the U.S.A., which leads to substantially tighter limits for exhaust emissions, particularly in California, and also from the development of a major new market in Europe. Platinum group metals catalysts are, and for some years will continue to be, the accepted means of controlling automobile tailpipe emissions. In order to meet the increasingly more stringent regulations, however, factors such as the warm-up characteristics and the high temperature durability of catalysts are receiving attention.

One means of achieving better performance is to reduce the cold start emissions; in the U.S. Federal Test Procedure much of the total emissions arise from this part of the test. One solution is to get faster catalyst warm-up by moving the catalyst system closer to the engine so that maximum use is made of the heat generated by the engine just after it is started. Subsequently, a catalyst in this position may experience substantially higher temperatures than in the conventional underbody position.

A paper by R. J. Brisley, R. D. O'Sullivan and A. J. J. Wilkins of Johnson Matthey, described the changes in performance of both platinum-rhodium and palladium-rhodium catalysts over 100 hours of engine running, when the inlet temperature to the catalyst was varied between 780 and 960°C. It was concluded that platinum-rhodium catalysts had the better resistance to thermal degradation at higher temperatures, when compared at the same platinum group metals loadings and ratio. However, an improved palladium-rhodium

catalyst with a higher palladium loading gave a similar performance to the standard platinum-rhodium catalyst, even at the highest ageing temperature of 930°C, except for the removal of nitrogen oxides which was still poorer.

In another paper M. J. Church, J. E. Thoss and L. D. Fizz of Johnson Matthey concluded that with platinum-rhodium catalysts, moving the catalyst to a hotter position did benefit performance, and that the gain in performance more than compensated for the increased deterioration caused by thermal ageing. Nevertheless, the authors suggest that there is a limit to the benefits that can be gained by increasing the operating temperature; temperatures in excess of 950°C should be avoided.

An alternative to mounting the catalyst close to the manifold is to heat the catalyst directly during a cold start. Several papers dealt with the use of heated metal substrates, in which the catalyst is heated by the application of electric power to the monolith upon which the catalyst is deposited. Papers by I. Gottberg, J. E. Rydquist, O. Backlund and S. Wallman of Volvo Car Corporation, in collaboration with W. Maus, R. Brück and H. Swars of Emitec; by W. A. Whittenberger, Camet Co., and J. E. Kubsh, W. R. Grace; and by M. J. Heimrich of Southwest Research Institute and S. Albu and J. Osborn, CARB, all showed the benefits of this system, particularly for hydrocarbon emissions control. However, the electric power necessary to reach the required catalyst operating temperature quickly is high; typical values of 4 to 5 kW were indicated. The in-use durability of heated metal substrate based catalysts is still largely unknown.

While it is generally agreed that platinum-rhodium and palladium-rhodium three-way catalysts are the best means of achieving the control of pollutants from cars, discussions continue about the development of the monoliths used as the catalyst support medium, with the objective of maximising the contribution the monolith makes to the performance of the whole catalyst. J. P. Day and L. S. Sucha of Corning analysed the substrate parameters influencing pressure drop and efficiency of the catalyst system, while M. Machida and J. Kitagawa of NGK Insulators, in collaboration with H. Yamamoto and F. Kato, Nissan, concentrated on the warm-up characteristics of thinner wall, low bulk density ceramic substrates. Metallic supports also received a lot of attention; F.-W. Kaiser and S. Pelters, of Porsche, compared the results obtained from a number of metal substrates with different cell densities, all coated with a similar platinum-rhodium catalyst formulation (5:1), at a loading of 50 g/ft³.

Control of emissions from diesel engine vehicles, especially particulate emissions, achieved a new prominence this year, with a number of sessions devoted to this subject.

With catalysed systems, aimed at in-situ regeneration, the common problem considered in many papers was the formation of sulphates arising from fuel-derived sulphur.

Catalysts which give good reduction of carbonaceous particulate matter are usually also good catalysts for further oxidation of the sulphur dioxide formed in the fuel combustion process. P. Zelenka of AVL, together with E. Lox and K. Ostgathe of Degussa offer the opinion that platinum-based catalysts provide the best guarantee of low tailpipe emissions and low rates of deterioration. This is due to their good performance at low temperatures (where the rate of sulphate formation is low), and their resistance to poisoning by oil additives. These authors conclude that, in addition to catalyst performance, careful optimisation of the engine combustion parameters is essential for success. Given the potential for better fuel economy, and hence reduced carbon dioxide emissions from diesel engines and their generally lower levels of gaseous pollutants compared with those for the corresponding petrol engines, interest in catalytic systems for the reduction of particulates and odours from diesel engines is likely to grow.

D.E.W.

Binary Coatings for DSA[®]-type Electrodes

Prior to the development of dimensionally stable electrodes (DSA[®]) in the late 1960s, the production of chlorine and chlorate via the electrolysis of brine generally made use of graphite electrodes. Graphite electrodes required frequent maintenance, but DSA[®] electrodes preserve both their shape and their voltage characteristics, and facilitate significant electrical power savings. They consist of a thin active coating, capable of catalysing the desired electrochemical reaction and of passing the electric current between a base metal support and the interface of the electrode with the electrolyte. The coating consists of a noble metal oxide mixed with a conducting or non conducting stabilising oxide, while the support is generally a valve metal such as niobium, tantalum, titanium or zirconium.

Such anodes have been considered for a variety of electrochemical processes, and a communication from the Swiss Federal Institute of

Technology, Lausanne, reports a systematic investigation of nine binary coatings made during the continuing search for a DSA[®]-type electrode suitable for oxygen evolution in concentrated sulphuric acid solutions (Ch. Cominellis and G. P. Vercesi, *J. Appl. Electrochem.*, 1991, 21, (4), 335-345).

On the basis of cost and performance titanium, which is used in most conventional DSA[®] applications, was selected as the base metal. The binary coatings consisted of a conducting oxide (RuO₂, IrO₂ or PtO_{0.12±0.05}) and a non conducting stabilising component (TiO₂, ZrO₂ or Ta₂O₅), and compositions ranging from 10 to 100 per cent of conducting oxide were tested. The results are discussed.

It was concluded that the titanium electrode coated with IrO₂ and Ta₂O₅, 70 and 30 mol per cent, respectively, was the best tested. It also displayed the best catalyst dispersion and gave the longest service life.