

## 40 Years of Cleaner Air: The Evolution of the Autocatalyst

**Autocatalysts have prevented billions of tonnes of pollution from entering the atmosphere and offer solutions to current concerns about urban vehicle pollution**

### By Chris Morgan

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The 40th anniversary of the manufacture of the world's first commercial batch of autocatalysts for passenger cars at Johnson Matthey Plc's site in Royston, UK, was marked in May 2014. Despite the enormous progress made in reducing the emission of pollutants from vehicles since the 1970s, there has also been considerable recent discussion about the levels of nitrogen oxides (NO<sub>x</sub>), especially nitrogen dioxide (NO<sub>2</sub>), and particulate matter (PM) in today's urban environment. This article describes the evolution of catalyst technologies over the last forty years and the next generation of products which will enable further advances in air quality.

### Initial Breakthroughs

From the 1940s onwards large cities, particularly in the USA and around Tokyo, were experiencing increasing levels of air pollution. In the 1950s work in California proved that photochemical smog formed from reactions between NO<sub>x</sub> and hydrocarbons (HCs) (1) and that internal combustion engine exhaust was a major source of such pollution (2). Clean Air Acts were passed in the UK and in the USA, and from 1968 all new passenger cars in the USA had to meet exhaust gas emissions standards. Initially these were achieved through better engine tuning, but an amendment requiring a further

90% reduction in emissions by 1975 forced the use of catalytic exhaust gas aftertreatment systems.

Johnson Matthey had been conducting research in the area since 1969, and in 1971 filed a patent for a rhodium-promoted platinum catalyst (3). This was used in a 'two-way' device, designed to remove the carbon monoxide (CO) and HC emissions caused by incomplete combustion of the fuel. Exhaust gas recirculation was used to control NO<sub>x</sub> emissions. Proof of durability was a critical step in the acceptance of the new technology. In 1972 Johnson Matthey demonstrated to the US authorities that a catalyst system still met the 1975 emissions standards after 26,500 miles of driving on a Chrysler Avenger (Figure 1) (4), helping to maintain the timetable for introduction of the legislation. In parallel, the introductions of lead-free gasoline and ceramic honeycomb materials that could support high temperature catalytic processes were also essential.

To achieve lower NO<sub>x</sub> emissions a dual-bed catalytic converter was developed (4). The engine was run rich, i.e. with an excess of fuel to generate reducing conditions, and NO<sub>x</sub> was reduced to nitrogen over the first catalyst. Secondary air was introduced into the exhaust to generate net oxidising conditions before the second catalyst, which was designed to oxidise CO and HC to CO<sub>2</sub> and water. While this system was effective it compromised fuel economy. The development of oxygen sensors in the late 1970s allowed the design of closed loop engine management systems which could accurately control the air to fuel ratio (AFR). This allowed the exhaust gas composition to be balanced at the optimum point for 'three-way' conversion: simultaneous oxidation of CO and HC and reduction of NO<sub>x</sub> over a single catalyst. Such three-way catalysts

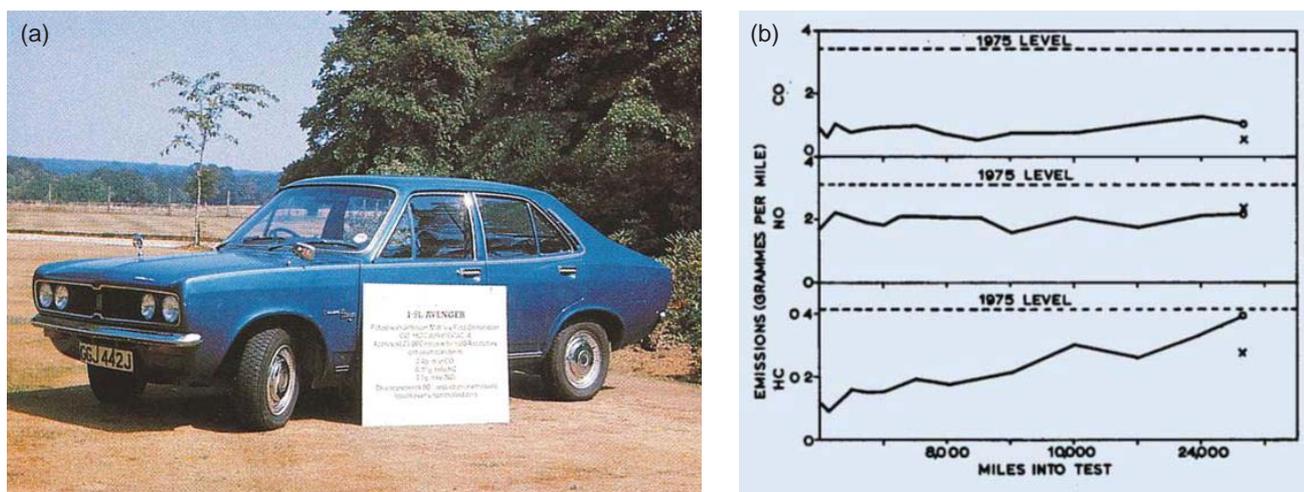


Fig. 1. (a) The Chrysler Avenger test vehicle; and (b) exhaust emissions obtained using the 1975 control system over 26,500 miles testing. (o = emissions at 26,500 miles before servicing of the vehicle, x = emissions at 26,500 miles after normal servicing of the engine, during which process the catalyst was not touched) (4)

(TWCs) were essential to meet another tightening of US emission limits effective from 1981.

### Developing Today's Catalysts

The early TWC designs are recognisable as the precursors to today's gasoline autocatalysts. There have since been major improvements in coating design, application of platinum group metals (pgms), thermal stability of raw materials and properties of the cerium-containing oxygen storage materials. Along with advances in engines and substrates, these have enabled increasingly stringent emissions limits and durability targets to be met on current gasoline vehicles around the world, whilst using substantially less pgms.

The emissions story in the US and Japan was focused primarily on gasoline vehicles, but in Europe, where passenger car emissions legislation was introduced in 1993, diesel engines had a significant market share. Heavy duty applications also predominantly used diesel engines. Diesel oxidation catalysts (DOCs) were effective in removing CO and HC emissions, but soot became a significant concern, especially in local low emission zones. In 1990 Johnson Matthey patented the use of NO<sub>2</sub> to reduce the combustion temperature of diesel soot (5). This technology was launched as the continuously regenerating trap (CRT®) in 1995, comprising a DOC to oxidise CO and HC and form NO<sub>2</sub> upstream of a cordierite particulate filter (6). This achieved much success as a retrofit device to control

emissions from local bus and truck fleets, and was later incorporated onto new vehicles. PM limits for diesel passenger cars did not require the fitment of filters until the introduction of Euro 4 legislation in 2005.

A limitation of the CRT® design was that each NO<sub>2</sub> molecule could only react once with the carbonaceous soot, requiring engines to be run at a high NO<sub>x</sub>:PM ratio. Incorporating pgm-containing washcoat into the filter walls, enabling 'used' NO molecules to be reoxidised to NO<sub>2</sub> *in situ*, allowed much more efficient filter regeneration at lower NO<sub>x</sub>:PM ratios. This was the basis of the catalysed soot filter (CSF) (7), now common in light and heavy duty diesel applications.

### The Future of Cleaner Air

Compared to those from 1974, today's vehicles have much cleaner and more efficient combustion processes, improved fuel injection system design and sophisticated engine management systems and sensing technologies. In conjunction with advanced catalyst technologies a modern passenger car typically emits one-hundredth as much pollution as one from ca. 1960. However, the impact of air quality on human health, particularly in urban environments, is high on the political agenda. Many European cities are breaching European Union limits on NO<sub>2</sub>, leading to renewed debate about local measures to reduce pollution (8). European real world driving emissions (RDE) legislation is being prepared, with the aim of ensuring that vehicle pollution is controlled over a wide

range of driving styles and ambient conditions, not just over the specified drive cycles. Meanwhile pollution is a major issue in many Asian cities, with, for example, Beijing considering the introduction of increasingly stringent emission limits.

The introduction of diesel particulate filters on light duty diesel (LDD) and heavy duty diesel (HDD) vehicles has been an important step towards addressing these concerns, supported by future legislation to control the number of particulates emitted (and not just their total mass) from gasoline direct injection engines in Europe and similar legislation expected for non-road mobile machinery. Selective catalytic reduction (SCR) is already a widely used technology to control NO<sub>x</sub> emissions from HDD applications in developed markets. Furthermore Euro 6 passenger car legislation, which came into effect in September 2014, more than halved the permitted NO<sub>x</sub> emissions from compression ignition engines, necessitating the introduction of specific NO<sub>x</sub> control technologies on almost all new European diesel passenger cars.

There are currently two competing technologies for diesel NO<sub>x</sub> control: SCR and NO<sub>x</sub> adsorber catalysts (NACs) (9), each with advantages and disadvantages. SCR systems, based on copper, iron or vanadium materials, reduce NO<sub>x</sub> to nitrogen through reactions with stored ammonia. High NO<sub>x</sub> conversion rates can be achieved and the reaction occurs under a standard diesel AFR, maintaining fuel economy. However, the ammonia is derived from the decomposition of urea solution injected into the exhaust gas upstream of the SCR catalyst. This requires an additional storage tank, urea injection and control system, the cost and space requirements of which can be prohibitive for smaller vehicles. The urea decomposition threshold temperature of ca. 180°C, limits the effectiveness of SCR systems in extended low temperature regimes such as low speed city driving in winter. There are also concerns about the release of excess ammonia into the atmosphere, leading to the development of additional ammonia slip catalysts (ASCs).

NACs trap NO<sub>x</sub> emissions during normal operation, typically by oxidation over a pgm and storage as nitrate on an alkaline earth such as barium. As the NAC has a finite NO<sub>x</sub> storage capacity, it is necessary to periodically regenerate the catalyst. This is achieved by running the engine rich for a few seconds to increase the concentrations of reductants including CO, HC and hydrogen in the exhaust gas. Under the rich conditions the nitrate decomposes and the

released NO<sub>x</sub> species are converted to nitrogen through reaction with the exhaust gas reductants over a second catalytic component, typically supported rhodium. The periodic requirement to run the engine rich adds to the complexity of the powertrain design and worsens fuel economy, which is undesirable given legislative targets to reduce CO<sub>2</sub> emissions/improve fuel economy. The additional cost of pgms can be a concern for larger vehicles. Furthermore there is a temperature window where NACs operate effectively: at higher temperatures the storage mechanism is less stable and at lower temperatures the NO<sub>x</sub> release and reduction reactions are less effective.

To address NO<sub>x</sub> control for RDE on diesel passenger cars a likely solution is a combination of NAC and SCR systems, harnessing the strengths of each technology. An upstream NAC will store NO<sub>x</sub> emissions at low temperatures when the SCR system is less effective. The NAC will also act as an oxidation catalyst to convert HC and CO emissions. A downstream SCR will provide NO<sub>x</sub> control under higher speed, higher temperature conditions, also enabling extended lean operation for improved fuel economy. Optimisation of such systems is taking place, with focus on matching the operating temperature windows of the NAC and SCR components.

As engines become increasingly fuel efficient less waste heat enters the exhaust. This is a critical concern for the aftertreatment system as it leads to lower catalyst operating temperatures. A common diesel catalyst architecture comprises a DOC followed by CSF, urea injection and SCR. Due to the thermal mass of the CSF (required to withstand uncontrolled soot regeneration) and heat losses from the exhaust pipe in the urea mixing zone in front of the SCR, it can take many minutes of city driving before the SCR warms up sufficiently to provide high levels of conversion efficiency. An elegant solution is to integrate the SCR coating onto the particulate filter (10), thus enabling the SCR coating to heat up and become active more quickly, whilst also improving the compactness of the system (**Figure 2**). Such SCR coated on filter (SCR<sup>®</sup>) technologies are now in series production – another world first for Johnson Matthey, Royston. Design challenges include the incorporation of significantly higher coating loadings onto a filter than were required for CSF, leading to a requirement for high porosity filter substrates and optimisation of the filtration efficiency and pressure drop characteristics.

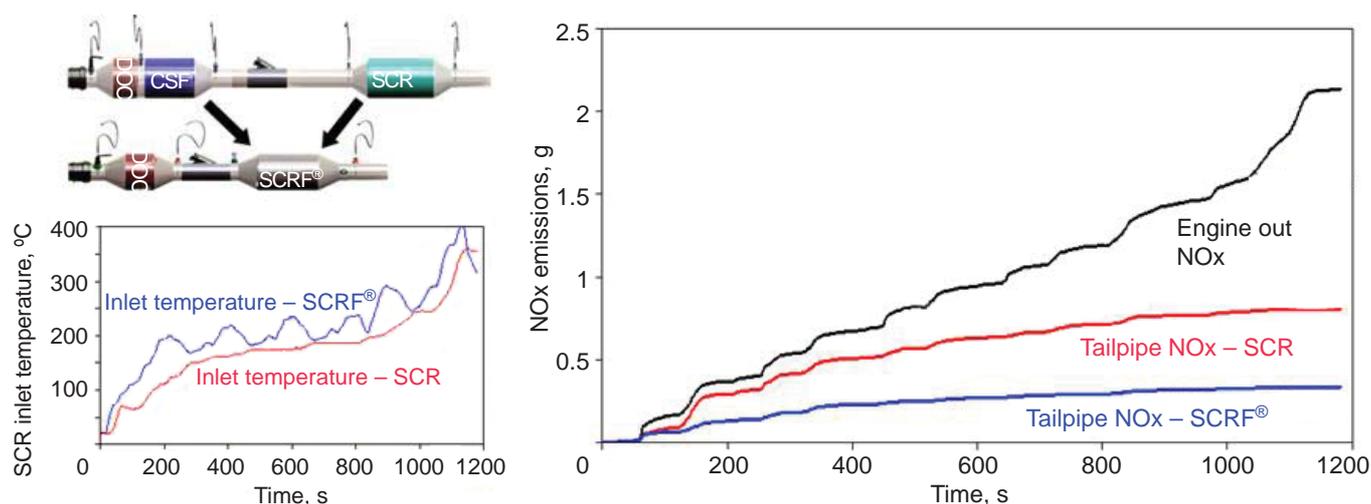


Fig. 2. Schematic demonstrating how the SCRf<sup>®</sup> improves system compactness and an example of how, over the European drive cycle, it warms up more quickly than an SCR downstream of a CSF (due to its closer proximity to the engine) enabling earlier NO<sub>x</sub> conversion

## Conclusions

Since the development of the first catalytic converters there have been many advances in powertrain, substrate and catalyst technologies over the last forty years. Emissions control systems are now required in countries across the world and they have prevented billions of tonnes of pollutants from entering the atmosphere. However, NO<sub>x</sub> and PM pollution continues to affect human health, particularly in urban environments. The introduction of new technologies to control diesel NO<sub>x</sub> emissions, alongside the more widespread fitment of particulate filters, will lead to further improvements in air quality.

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## The Author



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