



Autocatalysts

30 Years in the Development of Autocatalysts

When the first car to be fitted with a catalytic converter rolled off a production line in the USA in 1974, it was a huge landmark for both the platinum group metals markets and the global auto industry. Over the 30 years since then, the automobile catalytic converter has been responsible for tremendous improvements in air quality and for shaping much of the pgm industry as it stands today.

This article traces some of the milestones in the development of environmental legislation and the catalytic converter, from the smogs of California in the 1950s through to the present day.

California in the 1950s and 1960s – "and the sky is grey... "

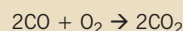
Emissions from motor vehicles had been recognised as a potential environmental problem in the USA from as early as the 1950s, when photochemical smog (with its characteristic grey-brown haze) was becoming a persistent feature of the Los Angeles basin in California. Tokyo and other large metropolitan areas also later suffered from similar pollution problems.

Research in California showed that the process of smog formation was complex but that it involved nitrogen oxides (NOx) and hydrocarbons (HC) reacting in sunlight to produce ozone. As air quality deteriorated, politicians began to take note of the issue and in 1963 the US Clean Air Act was passed. This first attempt to control atmospheric pollution in the USA set standards for stationary source emissions, such as those from power plants and factories. However, measurements showed that automobiles were responsible for 70 per cent of the HC emissions and 60 per cent of the NOx emissions in the air. Consequently, the Clean Air Act amendments of 1965 (the US Motor Vehicle Air Pollution Control Act) were adopted and set the first federal emission standards to control pollution from automobiles, beginning with 1968 models. The standards set were a 72 per cent reduction in HC and a 57 per cent reduction in CO from 1963 levels and were to be effective for 12,000 miles using fuel containing 3 grams of lead per gallon.

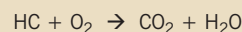
The Pollutants and Chemistry of Emission Control

The main pollutants from vehicle exhausts are hydrocarbons (HC), formed by the incomplete combustion of the fuel and encompassing a wide range of organic compounds such as methane, aromatics, oxygenates, etc; carbon monoxide (CO); and oxides of nitrogen (NOx). Carbon dioxide and water are also emitted and, particularly in the early years, lead, sulphur and phosphorus compounds were present.

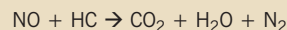
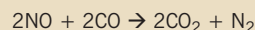
In simple terms the reactions that occur within a three-way catalytic converter are the oxidation of carbon monoxide to produce carbon dioxide:



the reaction of hydrocarbons with oxygen to produce carbon dioxide and water:



and the conversion of nitrogen oxides to nitrogen via reduction reactions with carbon monoxide and hydrocarbons:



Several catalyst systems from US manufacturers were selected for evaluation but their durability was severely limited by the high lead content of the fuel, which acted to rapidly deactivate (poison) the catalyst. Furthermore, the car industry was not enthusiastic about fitting 'add on' devices manufactured by others, and through the use of engine modifications auto makers were able to meet the required standards without the use of catalysts. However, the driveability and fuel economy of US cars with such engine modifications were poor by any criteria and the air quality, particularly in California, continued to deteriorate as the number of cars on the road increased.

Concern for the environment amongst the general public (and

1950's ...

■ Work by Dr. Arie Haagen-Smit at the California Institute of Technology proved that automotive exhaust emissions were a major source of photochemical smog in Los Angeles.



1965 ...

■ The US Motor Vehicle Air Pollution Control Act (amendments of the Clean Air Act) set the first federal emission standards to control pollution from automobiles, beginning with 1968 models. The targets were met without catalysts.

1970 ...

■ An estimated 20 million people participate in 'Earth Day' events in the USA. Subsequently, the US Environmental Protection Agency (EPA) is established and US Congress passes a major revision of the Clean Air Act (1970 amendments) incorporating substantially lower vehicle emissions limits. Agreement to phase out lead in gasoline in the USA from 1972 onwards.



1971 ...

■ Johnson Matthey files a patent covering the use of a rhodium-promoted platinum catalyst to control NOx and gaseous organic compounds.





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enlightened politicians) in the USA increased throughout the late 1960s, culminating in Earth Day in April 1970. This event contributed directly to the passing of the 1970 Amendments to the US Clean Air Act by the US Congress and to the establishment of the US Environmental Protection Agency (EPA) a few months later.

The 1970 Clean Air Act amendments required car emissions of HC, CO and NOx to be reduced by at least 90 per cent from 1970/71 levels by 1975/76. It appeared that engine modifications alone would be unlikely to meet these much tougher standards and so a real opportunity emerged for the introduction of catalysts on cars.

1970s – Rapid progress in catalyst development

The 1970 US Clean Air Act legislated for control of all three major pollutants but catalysts were only required to control HC and CO – it would be some years before catalytic control of NOx would become necessary. Nevertheless, the obstacles to developing a successful oxidation catalyst that could operate in an engine exhaust system were considerable, and were compounded by the fact that car manufacturers were adamant that no significant engine modifications would be made to overcome catalyst limitations.

The relative cost of pgm caused many car companies to initially favour catalysts formulated with base metal compounds such as copper chromite. However, a major problem for catalyst engineers was the high emissions that occur when a car is started from cold; the catalyst needs to reach its operating or 'light-off' temperature before it starts to work. Compared with platinum-based catalysts, base metal formulations performed poorly, requiring higher light-off temperatures and so taking longer to start converting pollutants effectively. In addition to their inferior catalytic activity, base metal catalysts were also highly susceptible to poisoning by sulphur present in the fuel and were unable to meet the required durability criteria. Although pgm can also be poisoned by sulphur, the effects are much more subtle and less problematic.



The Mark I Volkswagen Golf, launched in the USA in 1974 as the 'Rabbit', was one of the first mass produced cars to be fitted with a catalytic converter.

With experimental work focussed on pgm catalysts, researchers then discovered that the concept of promoting platinum with other metals could produce catalysts with superior light-off performance to platinum-only catalysts. The most effective promoters were found to be other platinum group metals, and platinum-rhodium and platinum-palladium catalysts became the frontrunners in the race to meet the US regulations.

Catalysts confirmed as the solution to pollution

Although the North American car industry was not enthusiastic about the proposed Clean Air Act legislation, vehicle manufacturers were required by the EPA to demonstrate that they had made a determined effort to meet the 1975/76 standards. In 1972 the EPA held the first of several hearings to assess progress to which the public and media were invited.

At the hearings, some vehicle manufacturers voiced doubts that the emissions limits could be met. However, Johnson Matthey had

1972...

■ Corning develops cordierite ceramics with high temperature and thermal shock resistance for catalyst monoliths. Johnson Matthey proves to the EPA that the US emissions regulations can be met using rhodium-platinum catalysts.



1974...

■ Effect of Middle Eastern oil embargo intensifies; US Congress sets the first fuel economy goals for automobiles, starting with 1975 models. The first catalyst substrates, with 200 cells per square inch (cpsi) and walls of 0.3 mm thick, are shipped to autocatalyst manufacturers.

1975...

■ The first cars fitted with oxidation catalysts reach showrooms in the USA; unleaded gasoline is widely available.

1976...

■ Japanese vehicle emissions standards to control HC, CO and NOx come into effect.



1977...→

■ US Clean Air Act amendments agreed to tighten emissions standards further from 1981 onwards.



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previously demonstrated to the EPA that vehicles fitted with a platinum-rhodium catalyst could successfully meet the required criteria. The EPA subsequently reaffirmed the timetable for the introduction of the standards, a ruling that was widely reported in the media at the time.

With the effectiveness of the catalyst proven in practice, work then began in earnest on developing a suitable support for the catalyst in the exhaust system and an economically viable production process. At the same time, research continued on further improvements to pgm catalyst technology.

Support from substrates

The successful introduction of auto catalysts was dependent on the development of a supporting material (or substrate) that could cope with the extremely demanding vehicle exhaust environment: the temperature can vary from ambient up to 1,000°C and can swing rapidly from one extreme to another; there are pulsations from the engine; the exhaust system vibrates; the gas mixture reaching the

catalyst varies; and when catalysts were first introduced there was significant residual lead in fuel as well as high levels of sulphur and phosphorus compounds.

The major breakthrough came when Corning Inc. licensed extrusion technology from ICI and used it alongside technology involving a magnesium aluminium silicate ceramic known as cordierite ($Mg_2Al_4Si_5O_{18}$), which was known to have a very low coefficient of thermal expansion. This enabled the production of bricks or 'monoliths' with a honeycomb structure that had a sufficiently high melting point and the thermal durability to withstand the tough operating environment, and that were relatively inexpensive to produce. The early, extruded monoliths had channels, or 'cells', with a square cross section and were produced with cell densities of 100 or 200 cells per square inch (cpsi), with a wall thickness of 0.3mm.

There were strong indications that reactions in exhaust catalysts would be quickened by increasing the surface area of the monolithic supports. It was not long, therefore, before ceramic monoliths with 300 cpsi, 400 cpsi and even higher numbers of cells per square inch with thinner walls became available from both Corning and NGK of Japan, which had also entered the market. In the late 1970s, metallic substrates derived from ultra-thin foils also became available. These were manufactured from corrosion-resistant steel only 0.05mm thick, allowing high cell densities to be achieved.

Although the monoliths had high surface to volume ratios, their intrinsic surface area was still too low to enable the active catalytic metals to be adequately dispersed. It was therefore necessary to apply a coating to the cells to increase the surface area. After extensive test work on a number of materials, alumina proved to be the best choice due to its chemical and physical characteristics, widespread availability and relatively low cost.

Coating the monolith

Having identified the most suitable high surface area material, it was then essential to develop technology to apply this to the monolith. The overall principle was to make a slurry of alumina in water, apply it to the monolith as a 'washcoat', and then dry and

The Evolution of Emissions Standards in the USA
(grams pollutant per mile)

| Vehicle model year | HC | CO | NO _x |
|-------------------------------|-------|------|-----------------|
| Pre-Control | 9.0 | 90.0 | 3.1 |
| 1975 | 1.5 | 15.0 | 3.1 |
| 1977 | 1.5 | 15.0 | 2.0 |
| 1981 | 0.41 | 3.4 | 1.0 |
| 1993 (California) | 0.25 | 3.4 | 0.4 |
| 1994 US Tier 1 | 0.25 | 3.4 | 0.4 |
| 1994 TLEV | 0.125 | 3.4 | 0.4 |
| 1997 TLEV | 0.075 | 3.4 | 0.2 |
| 1997 – 2003 ULEV | 0.04 | 1.7 | 0.2 |
| 2004 ULEV2 | 0.04 | 1.7 | 0.5 |
| 2004 – 2007 SULEV2/US Tier II | 0.04 | 1.7 | 0.2 |



The ongoing tightening of emissions regulations continues to drive autocatalyst development and strongly influences pgm consumption.

.....→ LATE 1970's ...

■ Ceramic monolith cell density improved to 400 cpsi and cell wall thickness is reduced to 0.15 mm. Ultra-thin metal foil substrates introduced. Increased substrate surface area helps to improve the pollution conversion efficiency of catalysts.



1981 ...

■ To meet the strict NO_x limits under the amended Clean Air Act, more sophisticated 'three-way' catalytic converters together with on-board diagnostic systems including oxygen sensors are introduced.

EARLY 1980's ...

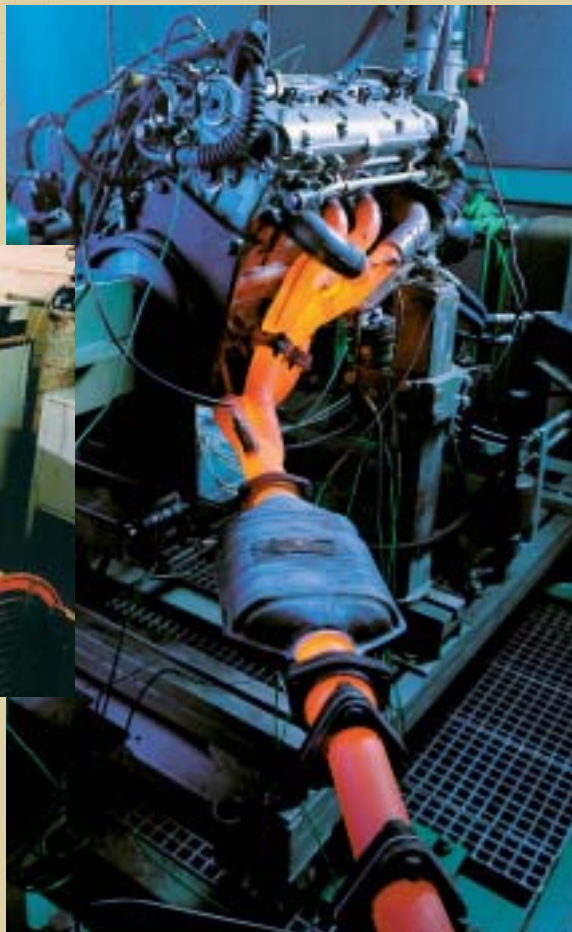
■ Performance of three-way catalytic converters significantly enhanced by use of improved oxygen storage materials (based on cerium dioxide) in catalyst washcoats. Vehicle emissions regulations introduced in Australia and Germany.





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calcine the catalyst in order to fix the washcoat to the support. Applying washcoats throughout the narrow channels within the monoliths and then clearing the excess was a significant challenge; it was important to prevent too much narrowing of the channels or indeed complete blockage, whilst obtaining strong adhesion of the washcoat to the substrate.



Tests on a Chrysler Avenger in the early 1970s were instrumental in proving that catalytic converters could be effective and durable. The science of catalyst research and testing has come a long way in 30 years.



The next requirement was to add accurately controlled amounts and ratios of platinum group metals. Not surprisingly, researchers discovered that different metal preparations could give vastly different catalyst performance, depending upon the interaction with the support. Various proprietary techniques were adopted by different catalyst manufacturers to introduce accurate quantities of pgm to the substrate, all of which required sophisticated chemistry to control the properties of the coating during its application. High volume manufacturing processes were successfully developed and commercial production of catalysts began in 1974.

The catalyst for cleaner fuels

Sulphur poisoning was instrumental in the failure of base metal catalysts but was considered less important to the first precious metal catalysts. The more problematic poisons for precious metal catalysts were lead and phosphorus compounds in fuel. Catalyst

resistance to both could be improved by adjusting washcoat formulations but for the catalytic converter to keep operating successfully over the required mileage the lead and phosphorus content of gasoline had to be reduced to trace levels. The EPA consequently instituted the first regulations for the effective phase out of lead and phosphorus additives in gasoline in 1973. At that time the average lead content in gasoline in the USA was 2 to 3 grams per gallon, resulting in around 200,000 tonnes of lead being emitted from vehicle exhausts every year. By 1996, when the sale

1990 ...

■ Further amendments to Clean Air Act in the USA require greater reductions in HC, CO, NO_x and particulate emissions from 1994 onwards (referred to as Tier I standards). Johnson Matthey files a patent covering the use of NO₂ to reduce the combustion temperature of diesel particulate matter in a filter, a system subsequently commercialised as the Continuously Regenerating Trap™.



1991 ...

■ New legislation introduced in Japan sets much more stringent vehicle NO_x emissions limits.

1993 ...

■ European Union emissions regulations that necessitate the use of catalytic converters (Euro I) come into effect.

1994→

■ Phase in of Tier I emissions standards begins in the USA.





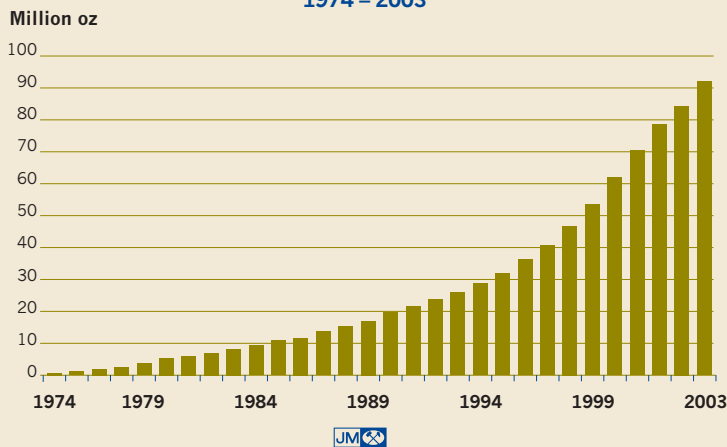
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of leaded fuel for on-road vehicles was eliminated completely, emissions of lead had dropped to less than 2,000 tonnes per year – a direct beneficial consequence of the introduction of catalytic converters.

With the introduction of increasingly tighter emissions regulations, attention later switched to the sulphur content of fuels and its long-term deleterious effect on the efficiency of catalytic converters. The more recent introduction of clean-burning low and ultra-low sulphur fuels has been integral to advances in the performance of automobile catalysts, and will be crucial to achieving substantial cuts in the emissions of particulate matter from diesel powered vehicles in future.

During its first 30 years the autocatalyst industry consumed over 90 million oz of pgm.

**Cumulative Automotive Industry Purchases of PGM
1974 – 2003**



Disproving the scare stories

During the early days of vehicle emission control, there was some opposition to the introduction of catalysts, both on the part of the auto industry and the public. There was a perception that catalysts imposed significant back-pressure on vehicle exhaust systems and caused poorer performance and fuel economy. What was often overlooked was that, before catalysts, engine modifications were the only way to meet

emissions legislation and it was these that often reduced performance.

A number of scare stories arose around exhaust catalysts and each of these had to be treated seriously. Catalysts were accused of starting forest fires and emitting cyanide, sulphuric acid and precious metal particles, amongst other things. Whilst some of these claims (cyanide emissions for example) were readily disproved, others such as sulphuric acid emissions required significant work in order to prove that the fears were groundless.

Tightening regulations push catalyst development

From the mid-1970s onwards the tightening of auto emissions regulations stimulated major advances in catalyst design. With air pollution in Tokyo reaching uncomfortable levels, tough exhaust emission regulations were introduced by the Japanese government and came into effect on 1976 vehicle models. The following year, further amendments to the US Clean Air Act (to be applied from 1981 vehicle models onwards) tightened the standards for HC and CO emissions and, most significantly, included tough new targets for emissions of NOx. Work on developing catalysts that could simultaneously oxidise CO and HC to carbon dioxide and water while also reducing NOx to nitrogen ('three-way' catalytic converters) accelerated as a result.

One of the keys to the successful commercial introduction of three-way catalysts in 1981 was the development of the oxygen sensor. The ability of three-way catalysts to deal effectively with CO, HC and NOx is heavily dependent on the ratio of air to fuel in the engine being maintained at an optimum balance for the conversion of all three pollutants. The introduction of oxygen sensors enabled engineers to design closed-loop engine management systems that could precisely monitor and control the mixture of air and fuel.

Further advances were made with the advent of oxygen storage materials, which were incorporated into the catalyst washcoat. Under rich conditions (excess fuel) these materials release oxygen to facilitate the oxidation of CO and HC. Under lean conditions (excess air) they enable NOx reduction by storing oxygen. Cerium dioxide was found to be a highly effective oxygen storage material and also promoted much

...→ 1996 ...

■ European Union emissions regulations tighten as Euro 2 standards are applied. Californian Low Emission Vehicle (LEV) standards come into force, emphasising the cold-start control of emissions; palladium-based catalysts found to be particularly suited to controlling HC emissions on engine start-up.

1998 ... 1999 ...

■ Ceramic substrates of 600 cpsi introduced, wall thickness reduced to 0.075 mm.

■ National Low Emissions Vehicle (NLEV) emissions standards take effect in the USA, requiring very substantial reductions in NOx.



2000 ...

■ Catalyst substrates with 900 cpsi and ultra-thin walls of 0.05 mm enter production for 2001 model year vehicles. Metal foil substrates available at up to 1,000 cpsi and with 0.025 mm thick walls. EU emissions standards for all road vehicles become more stringent with introduction of Euro 3 regulations.



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higher catalytic activity for the conversion of CO and NOx.

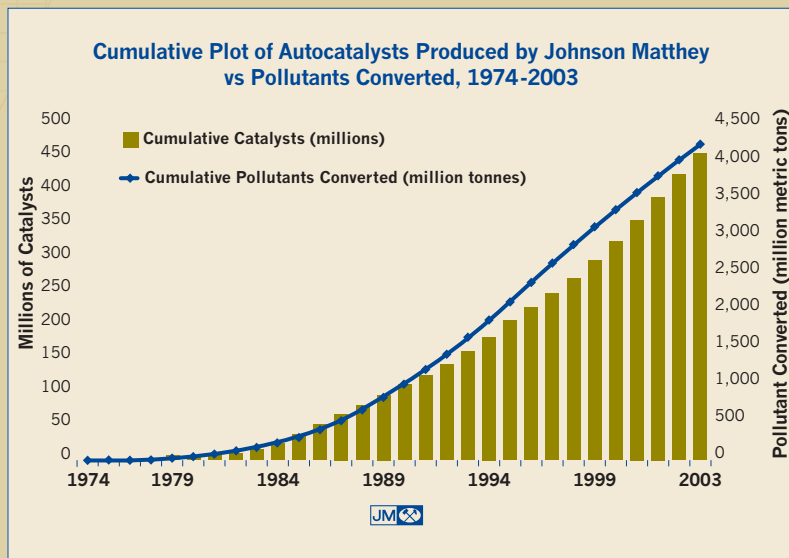
Research and development of improved catalytic converters progressed throughout the 1980s and early 1990s as emissions control legislation continued to tighten in the USA and spread to countries such as Germany and Australia. Assisted by the sophisticated surface analysis technique of X-ray photoelectron spectroscopy, the industry began to gain a deeper understanding of what happens to multi-metal catalyst in use. In particular, this work raised the question of whether the physical separation of platinum and rhodium within a catalyst would improve its performance.

Trials showed that catalysts in which the two metals had been deliberately separated from each other resulted in lower emissions. This led to the design of catalysts in which the distribution of pgm within the structure of the catalytic layer was closely controlled. The first of these structural catalysts came into use in the early 1990s and, through their improved thermal stability and more rapid light-off, helped to significantly improve catalyst performance.

Coming up to date

The control of vehicle emissions became increasingly widespread during the 1990s as regulations that necessitated the fitment of catalytic converters were introduced in the European Union, Mexico, Brazil, India, Malaysia and Thailand. Existing regulations in the USA and Japan also became progressively more stringent and substantial reductions in particulate matter emissions were increasingly mandated. These factors, together with the constant pressure from auto makers to minimise the cost of emissions control systems, were and are the driving forces behind catalyst development.

Today it is possible to produce catalysts on ceramic substrates with as many as 900 cells per square inch and walls less than 0.05mm thick, whilst metallic substrates of 1,000 cpsi and walls of only 0.025mm thick are available and offer the ability to produce complex internal structures. Catalysts with exceptional thermal durability can now be mounted very close to the engine manifold, whilst the control of pgm distribution on the catalyst has become even more sophisticated. Advances such as these have allowed engineers to keep abreast of ever tightening emissions legislation through



improving catalyst performance whilst at the same time also enabling significant reductions in average pgm loadings.

Johnson Matthey has produced over 450 million autocatalysts since 1974, which have converted more than 4 billion tonnes of pollutants into harmless gases.

Conclusion

In 1960 a car would typically pump out over 100 grams of CO, HC and NOx for every mile driven. Today, a new car bought in the USA, Japan or Western Europe will only emit around 2 grams of these pollutants per mile. The ability to achieve exhaust emissions that are close to zero from today's cleanest cars is the result of more than three decades of research and development by automotive manufacturers, catalyst companies, and substrate suppliers in response to ever more demanding environmental legislation.

The permissible limits on auto emissions will continue to tighten over the next few years in already highly regulated markets such as the USA and Europe. In countries where car ownership is rapidly increasing, China and India for example, legislation is catching up quickly. In addition, emissions regulation of the heavy-duty diesel sector is set to become tougher and more widespread. These trends will drive even further enhancements in catalyst efficiency whilst providing new opportunities for the platinum group metals.

Acknowledgements
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2000-01 ...

■ The palladium price spike peaks at \$1,094 per oz.

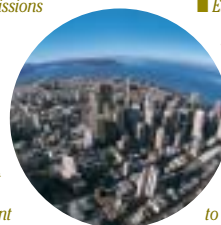


2003 ...

■ Strict particulate matter limits introduced for heavy-duty diesel vehicles operating in the Tokyo area, requiring a substantial programme to retrofit catalysed particulate filters. Diesel car sales in Europe surpass 6 million vehicles for the first time.

2004 ...

■ Phase in of US Tier II emissions standards begins. These mandate further large reductions in NOx and particulate matter emissions. Tier II compliant vehicles are up to 99 per cent cleaner than vehicles sold in the 1960s.



2005-08 ...

■ Euro 4 emissions regulations and new Japanese standards will apply to new vehicle models and will require further substantial reductions in emissions of all major pollutants, particularly particulate matter from diesels. Phase in of US Tier II standards to be completed; Euro 5 standards likely to be finalised; regulation of vehicle emissions in countries such as China, India and Russia will increase.