

Exhaust Purifiers for Compression Ignition Engines

CATALYTIC CONTROL OF DIESEL EXHAUST GASES

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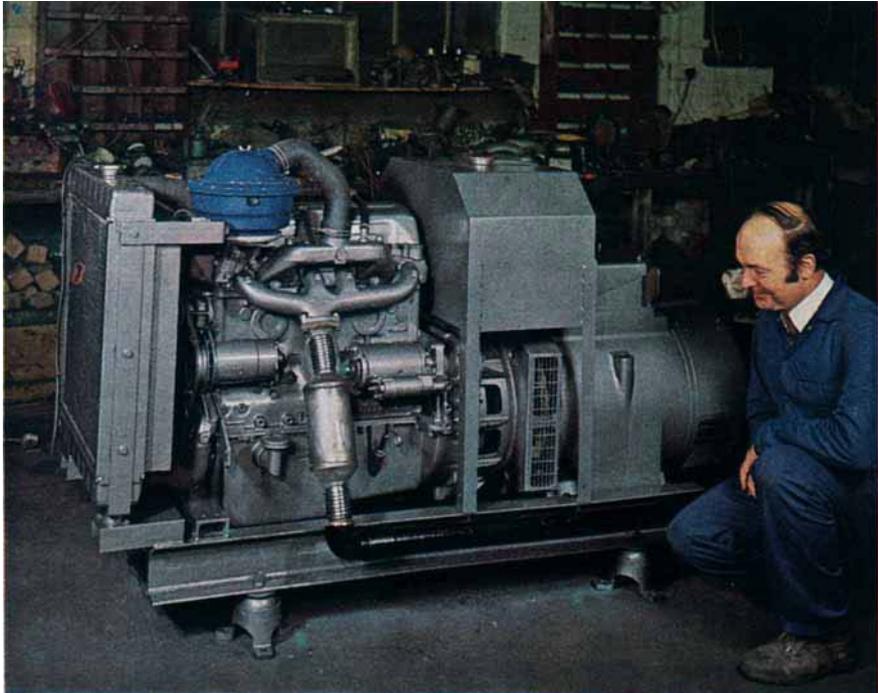
A new platinum catalyst system has been developed at the Johnson Matthey Research Laboratories for the oxidation of hydrocarbons and carbon monoxide emitted by compression ignition internal combustion engines. The catalyst was evaluated during tests on a direct injection diesel engine using the 13-mode cycle devised by the California Air Resources Board, thereby assisting the design of catalyst systems to meet specific emission control targets in particular industrial applications. The new catalyst combined with retardation of injection timing can provide overall control of exhaust emissions, including the nitrogen oxides, from diesel engines.

Compression ignition engines using diesel oil as fuel are widely used as motive power in road, rail, or sea transport and for haulage or lifting equipment in mines and factories. They range in size from small air cooled industrial units of less than 1 litre cylinder displacement volume to large marine engines of over 1500 l. The performance of these engines is highly dependent on the efficiency of the combustion process and considerable effort has been applied to the development of different types of combustion chamber in order to balance the need for fuel economy with the requirement for high power output. The small high speed diesel engines used in taxis, cars and other light duty vehicles are frequently based on an indirect injection (IDI)

system in order to give acceptable efficiencies over a wide speed range. These can compete with petrol fuelled spark ignition engines. The larger commercial vehicles are usually fitted with direct injection (DI) engines where adequate power is available without excessive fuel consumption. Both types of engine are highly reliable and can be operated for long periods without needing major servicing.

In some of these applications, such as mining, or inside factory and warehouse areas where engines are operating in confined spaces, it is necessary to ensure that exhaust emissions are not hazardous to health or to general safety. In contrast, emissions from engines used in marine applications can be freely discharged to the atmosphere without causing an immediate nuisance or health hazard. However, there is increasing public awareness of the direct and indirect harmful effects of all forms of environmental pollution. Therefore, extensive effort is being applied to develop practicable and economic methods for the control of pollution emanating from industrial manufacturing processes and from the combustion of fuel in engines used on mobile or stationary applications.

The pollution from internal combustion engines is due to the chemistry of the reactions taking place between fuel vapour and air mixtures during high temperature combustion and to the effects that engine design and engine operating conditions have on these reactions. Although this article is primarily concerned with diesel engines it is important to remember that there is no fundamental difference from the analogous pollution prob-



A Honeycat Diesel Exhaust Purifier unit forming part of the exhaust train of a Ford-Stamford 40 kVA diesel alternator set assembled by John S. Allen & Son Limited. This stationary generator is powered by a Ford model 2712E four cylinder diesel engine, which is coupled to a Stamford brushless alternator giving a 415 volt three-phase 50 Hz output. The set will be used within a building

lem for petrol fuelled engines. Therefore the principles governing application of catalysts to the control of engine emissions and some of the legislation are common to both spark and compression ignition engines.

Engine Exhaust Emissions

Exhaust gases contain the oxidation products from combustion of the hydrocarbon fuel and, if chemical equilibrium was reached, these products would consist almost entirely of carbon dioxide and water vapour. This would occur at high temperatures provided the fuel vapour plus (at least) the stoichiometric quantity of air was homogeneously mixed and the residence time was sufficiently long. In practice the combustion processes in an engine are extremely complex as fuel: air ratios and temperature can vary considerably according to the position in the combustion zone. Therefore the composition and the

concentration of individual components in the combustion products will vary considerably according to engine type and engine operating conditions. Typical exhaust from a petrol engine may contain up to 10 per cent carbon monoxide—due to the combustion process taking place at, or near to, stoichiometric air/fuel ratios—together with about 1000 p.p.m. hydrocarbons from unburnt fuel or partially oxidised products. In contrast a diesel engine operates with a large excess of air, which is sometimes increased by turbocharging, so combustion is more complete. Concentrations of 0.1 per cent carbon monoxide and 300 p.p.m. hydrocarbons are typical. Some sulphur dioxide may be present due to combustion of organic sulphur compounds in the fuel, particularly for diesel oils.

Diesel exhaust may contain up to 0.5 g/m³ particulate matter, which becomes very obvious as a dark smoke. This is due to

incomplete combustion, and smoke formation is favoured by high pressures, high temperatures and low oxygen availability. Black smoke due to presence of carbonaceous material must be distinguished from the white smoke caused by unburnt fuel droplets and from the blue smoke due to combustion of lubricating oil. Smoke formation does not normally occur to any significant amount in a properly maintained petrol engine.

The temperature of combustion in both compression and spark ignition engines is high enough to cause formation of nitrogen oxides (NO_x) from the nitrogen and oxygen present in the air used for combustion, and up to 4000 p.p.m. NO_x may be present in exhaust gases. In a direct injection engine the formation of NO and smoke is highly dependent on the conditions in the vicinity of the fuel injection nozzle and on the degree of air/fuel mixing in the swirling action caused by the geometry of the combustion chamber. Conditions which favour minimum smoke formation tend to promote NO formation and, therefore, design of the combustion zone and fuel/air inlet arrangements has to be a compromise. Until recently emphasis has been placed on minimising smoke formation.

The distinctive obnoxious odour of diesel exhaust gases is a well known nuisance. It should not be considered as a separate emission because it is entirely due to the presence of oxygenated compounds produced by partial oxidation of certain fuel fractions and is, therefore, included with hydrocarbon emissions. Thus any method that reduces these emissions or promotes complete oxidation to carbon dioxide and water will help eliminate odour.

Legislation

The United States, Canada, Japan, South Africa, and many European countries, including the United Kingdom, have introduced legislation designed to limit the emission of smoke from diesel engines used on road vehicles. Precise limits, test procedures, and methods of enforcement vary considerably. Experience in the United Kingdom has shown that although it is possible to ensure that new engines, as delivered from the manufacturer, meet the regulations there are very obvious failures under actual use conditions, particularly when heavy transport vehicles are working under maximum load. Until relatively recently no country has

Table I
American Legislation for Exhaust Emissions

Regulation	Date*	Test Method	Emission Limits				Units
			HC	CO	NO_2	HC+ NO_2	
California, heavy duty vehicles	1973-74	CARB	—	40	—	16	g/bhp/h
	1975-76	CARB	—	30	—	10	g/bhp/h
	1977	CARB	—	25	—	5	g/bhp/h
California, light duty vehicles	1975	CVS	0.9	9.0	2.0	—	g/mile
California, light duty trucks	1975	CVS	2.0	20.0	2.0	—	g/mile
U.S. Federal, heavy duty vehicles	1974	CARB	—	40	—	16	g/bhp/h
U.S. Federal, light duty vehicles	1975	CVS	0.41	3.4	3.1	—	g/mile
	1976	CVS	0.41	3.4	0.4	—	g/mile
U.S. Federal, light duty trucks	1976-77	CVS	2.0	20	3.1	—	g/mile

* Some of these regulations are not yet finalised but have been proposed for the dates shown

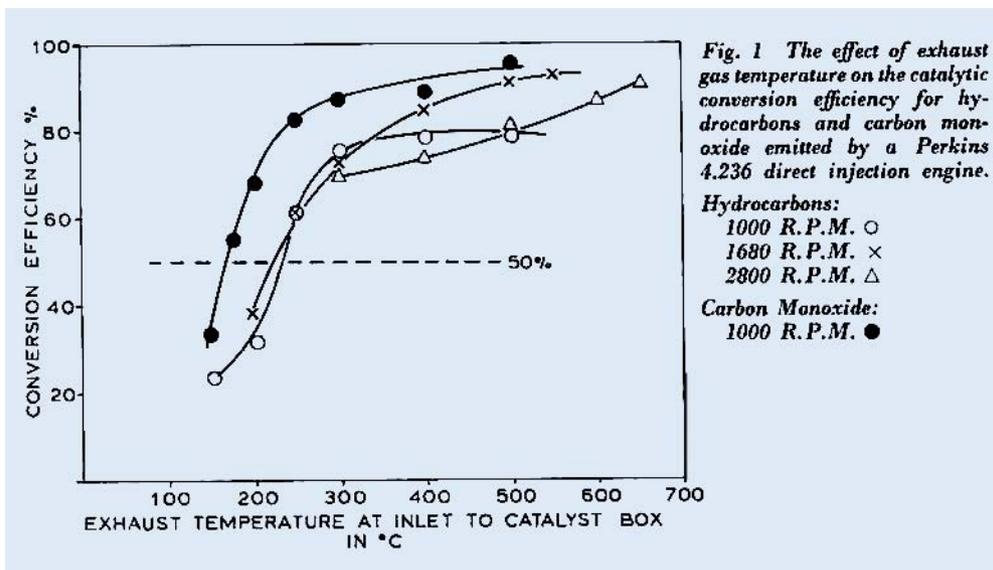


The elimination of noxious emissions from equipment used in tunnel construction is obviously necessary to safeguard the health of those engaged in the work. This dump truck owned by Southdown Plant Limited has been fitted with a Honeycat DEP unit before use by Tube Headings Limited in driving a tunnel beneath a main road in north London

attempted to limit other emissions by legislation but pollution in the United States, particularly in California, has caused that country to consider the overall pollution problem in considerable detail and to propose regulations (some of which are now becoming legally operative) for all types of road vehicle. Table I shows the emission limits defined in U.S. Federal and California State regulations for various types of vehicle. For heavy duty vehicles (which usually use diesel engines to supply motive power) the total brake specific emissions for a 13-mode steady state cycle are determined by means of a weighted summation of mass emissions determined for each mode. This cycle has been defined by the California Air Resources Board and is conveniently referred to as the CARB cycle. U.S. Federal regulations for heavy duty

diesel and petrol powered vehicles over 6000 lb. (approx. 2.7 tonnes) gross vehicle weight use the same test cycle with slight modification of experimental conditions. Federal limits for diesel light duty vehicles are based on a constant volume sampling (CVS) cycle as used for the 1972 petrol engine regulations.

It may be possible to meet all these targets for road vehicles by engine modifications (and much development effort has been applied by manufacturers to achieve this) but it is believed that the very low combined figure of 5 g/bhp/h for HC and NO_x may be quite difficult to obtain and maintain under actual service conditions. In this and other special cases, such as when engines are used in confined spaces where ventilation may be inadequate, additional means of control may be necessary. Catalytic oxidation is a proven



system (1) that is being applied to the analogous problem on petrol engined vehicles which are now becoming subject to stringent exhaust regulations in certain countries. Similar systems developed (2) in these laboratories have also already been used in diesel engine applications but lack of effective legislation has not given users sufficient incentive to abate the pollution from this source.

Properties of Oxidation Catalysts

Recent work in these laboratories has led to the development of an improved type of platinum group metal catalyst which can be supported on a refractory monolith and can be applied to the oxidation of diesel exhaust gases. The supported catalyst module is contained inside a sheet metal box similar in external appearance to a standard automobile silencer box. The overall system is known as the Honeycat[®] Diesel Exhaust Purifier (DEP).

A standard DEP unit taken from routine production was evaluated for control of emissions from a Perkins 4.236 (~4 litre) direct injection engine mounted on a dynamometer test bed. Emissions before and after the catalyst were measured by standard pro-

cedures (3). The essential properties of the catalyst are illustrated in Fig. 1 which shows the effect of variations in engine speed (and therefore volume of exhaust gases) and exhaust temperature on the conversion of hydrocarbons and carbon monoxide. Obviously the key factor which determines whether the catalyst will be effective is whether the temperature of the exhaust gases is above the ignition temperature (usually defined as t_{50} per cent) of the catalyst. Values as low as 150°C for carbon monoxide to about 225°C for hydrocarbons are typical of this catalyst. Therefore it is necessary to examine how exhaust temperature varies with operating mode on typical engines.

Diesel Exhaust Gas Temperatures

Exhaust temperatures vary considerably with engine load/speed combinations and with engine type. Values shown in Figs. 2 (a) and 2 (b) for direct and indirect injection engines illustrate the general trend. Increasing the load at a constant speed increases the temperature up to a maximum of 500–600°C. The isotherms also represent lines of equal conversion which may be predicted from the conversion data of the type shown in Fig. 1 for particular catalysts.

[®]Johnson Matthey Chemicals registered trade name

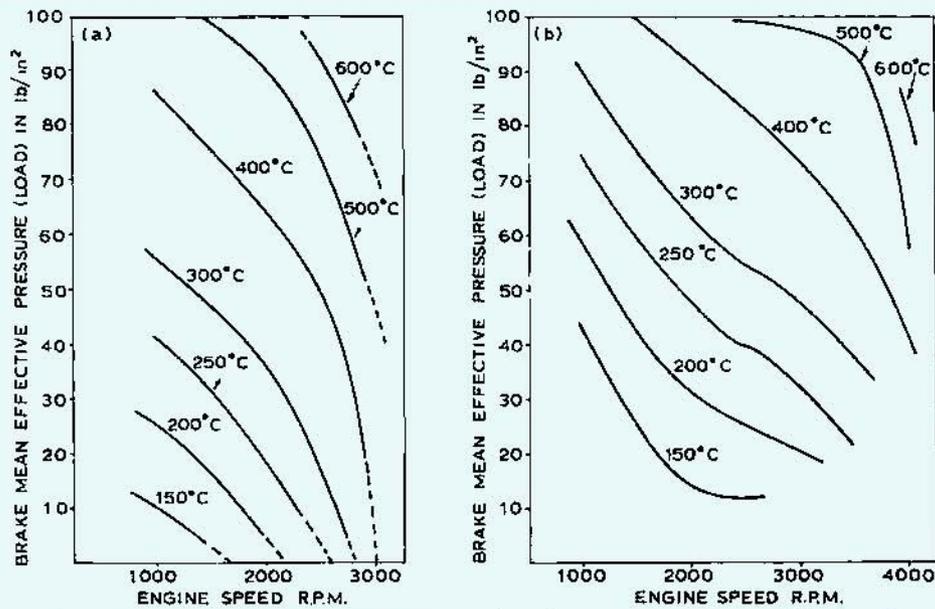


Fig. 2 The effect of engine load and speed on the exhaust gas temperature of diesel engines.
 (a) Direct injection engine.
 (b) Indirect injection engine

Effect of the Catalyst on Engine Operation

The effect of fitting a DEP unit into the exhaust system on fuel consumption, engine power, and smoke production is negligible, as shown in Fig. 3. The effect on exhaust back pressure will obviously alter with the cross-sectional area and volume of the catalyst chosen to meet particular emission control targets but the system used for these experiments doubled the back pressure.

Control of Carbon Monoxide and Hydrocarbons

The volume and composition of exhaust fume varies with engine operating condition. Hydrocarbon emissions show concentrations between 500 and 750 p.p.m. over the major part of the working range of the engine in the ex-works con-

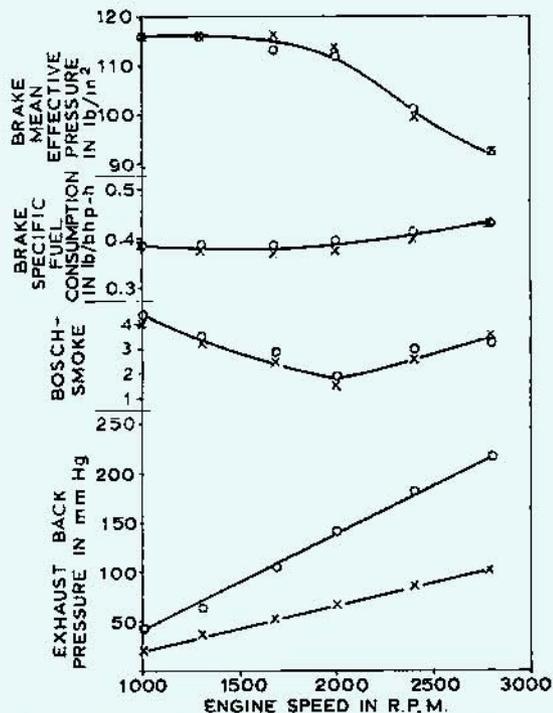


Fig. 3 The effects of fitting a diesel exhaust purification unit into the exhaust system on engine power (brake mean effective pressure), fuel consumption and smoke production are negligible. In this case the fitting of the catalyst system doubled the back pressure.
 ○ With catalyst; × without catalyst

Engine Mode	Per cent Full Power	Emissions, g/h			
		Hydrocarbons		Carbon Monoxide	
		Before Catalyst	After Catalyst	Before Catalyst	After Catalyst
Idle*	0	24	18	22	21
Intermediate Speed (1680 r.p.m.)	2	70	56	57	11
	25	59	24	68	9
	50	51	11	67	6
	75	46	5	78	12
	100	44	2	403	57
Rated Speed (2800 r.p.m.)	100	62	6	489	14
	75	93	14	318	17
	50	97	21	252	17
	25	115	31	291	23
	2	151	48	212	17
Brake specific emissions, g/bhp/h		2.52	0.78	6.8	0.7

* Average over the three idle periods for 13-mode cycle. Data obtained on 4.236 D.I. engine fitted with standard Honeycat Diesel Exhaust Purifier

dition, and less than 250 p.p.m. after catalytic treatment during the load/speed range where the catalyst is operating above ignition temperature. The absolute amount of emissions obviously increases with increase in engine speed and will be approximately

proportional to speed. There is only a limited area at virtually zero load where the catalyst is not able to operate due to insufficient temperature. Similar data is available for carbon monoxide and shows that, as expected, conversion efficiencies for this easily oxidised

Engine		Catalyst Geometry	Brake Specific Emissions, CARB Cycle, g/bhp/h							
Injection Type	Timing		HC		CO		NO ₂		HC+NO ₂	
			Before	After	Before	After	Before	After	Before	After
Direct	Standard	Type B	2.5	0.8	6.8	0.7	10.5	10.3	13.0	11.1
		Type L	2.2	0.8	6.8	0.9	10.3	10.5	12.5	11.3
Direct	12° retard	Type B	5.3	2.7	14.0	1.7	4.4	4.6	9.7	7.3
		Type L	4.9	2.3	10.6	1.4	4.3	4.6	9.2	6.9
Indirect	Standard	Type L	2.4	1.0	11.0	2.0	3.4	3.4	5.8	4.4

Type B elliptical cross-section
Type L circular cross-section; catalyst volume approximately 14 per cent smaller than Type B

molecule are higher than for hydrocarbons at corresponding temperature. Overall performance for hydrocarbon and carbon monoxide oxidation is demonstrated by emission measurements on exhaust gas samples taken before and after the catalyst installation during operation of the engine through the CARB 13-mode cycle referred to previously. Table II shows values for the 4.236 engine using a standard Honeycat catalyst. Table III summarises the CARB cycle specific emission data for DI and IDI engines using two catalysts of identical composition but with slightly different volumes chosen as convenient to fit commonly used round and elliptical cross section silencer boxes.

Control of Nitrogen Oxides

Table III shows that the catalyst has no significant effect on NO_x emissions. Any small apparent increase across the catalyst is not a real effect but is due solely to experimental error in sampling and analysis. It also shows that the NO_2 value is a major contributor to the combined $\text{HC} + \text{NO}_2$ limit value specified in certain American legislation. (Although NO_2 is used as a convenient method for expressing total NO_x emission, it should be noted that NO is the major component.) However, it is known that retarding injection timing will reduce NO_x formation. Unfortunately, as mentioned earlier, and shown in Fig 5, the conditions which help to prevent NO_x synthesis will lead to decreased combustion efficiency and, therefore, to an increase in the amounts of oxidisable components in the exhaust.

This technique of altering timing therefore suggests a method of NO_x emission control *provided* that catalytic systems are used to control the increased quantities of hydrocarbons and CO. Although a minimum value for $\text{HC} + \text{NO}_2$ occurred at about 8° retard the value of 12° retard, corresponding to minimum NO_x formation, was chosen to evaluate the catalyst system because this could only affect HC and CO. Comparison of the CARB cycle data of Table III for the diesel engine

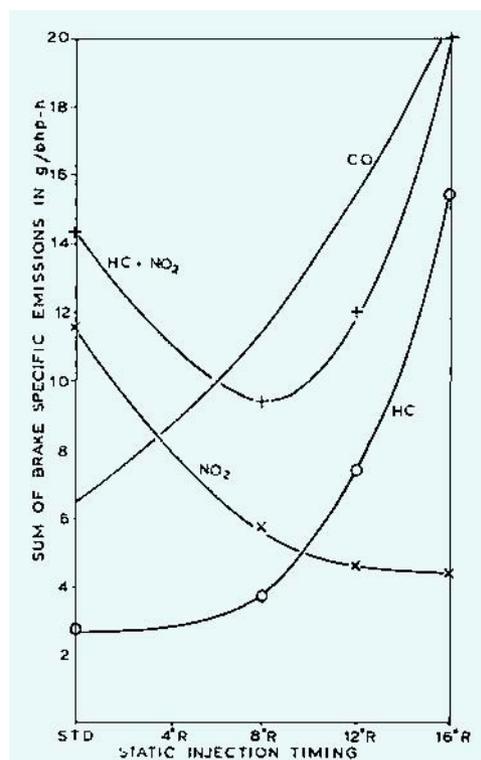


Fig. 5 Retarding the injection timing affects the emissions of hydrocarbons, carbon monoxide and nitrogen dioxide from the diesel engine. The catalyst is fitted downstream of the sampling point for this test

in standard and retarded timing shows that the catalyst will cope very efficiently with the increased emissions.

Odour Control

Accurate quantitative data on odour control is difficult to obtain as it is usually necessary to use organoleptic methods of assessment. The use of odour panels is expensive and time consuming but independent measurement of the efficiency of the Johnson Matthey catalyst using specially constructed air sampling cells and a trained panel of observers has demonstrated that the catalyst is an extremely effective method of odour control. Similar work, using successive dilution of exhaust samples taken by hypodermic syringe to determine odour threshold values (4), was done in our own research programme.

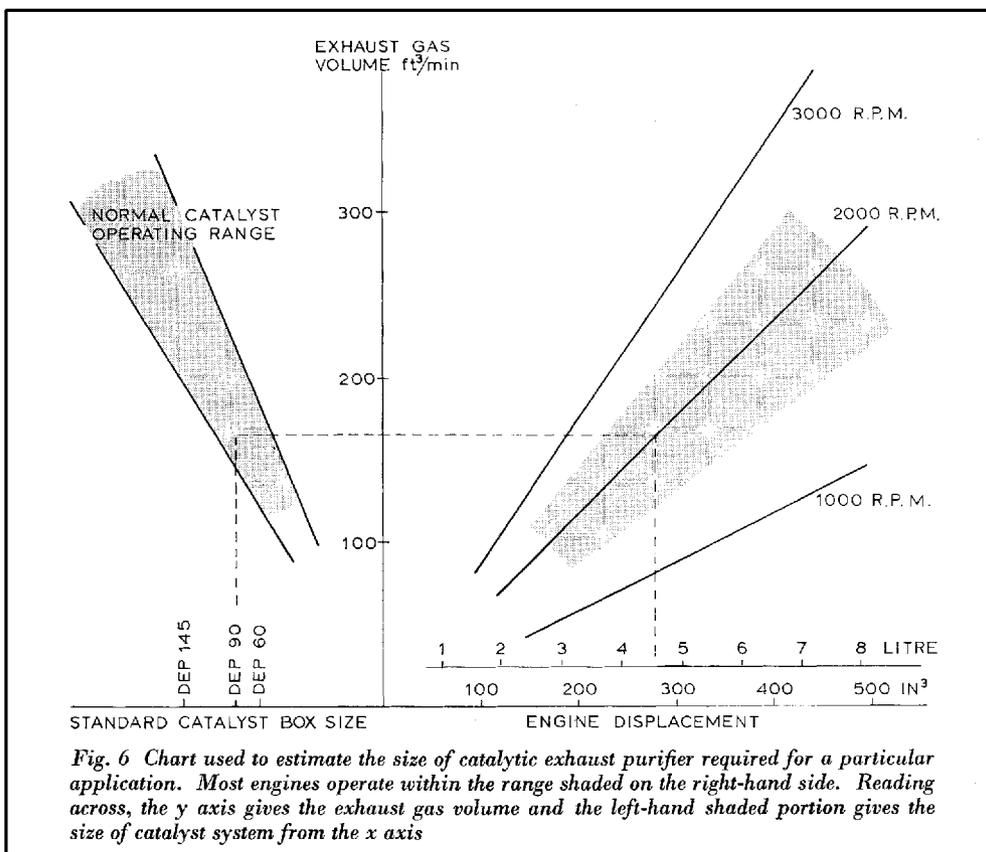


Fig. 6 Chart used to estimate the size of catalytic exhaust purifier required for a particular application. Most engines operate within the range shaded on the right-hand side. Reading across, the y axis gives the exhaust gas volume and the left-hand shaded portion gives the size of catalyst system from the x axis

Measurements of odour threshold were made during runs arranged as a 2×2 factorial experimental design (5), with centre point, in order to determine the amount of odour control possible for various load/speed engine conditions. These confirmed that the catalyst made a significant contribution to odour control at all times when exhaust gas temperature was above about 200°C . Even at engine idle, when temperatures were too low for catalytic ignition, some observers reported an improvement in odour. Further work on this topic is planned in which organoleptic and instrumental methods of odour measurement will be used simultaneously.

Application to Diesel Engine Plant or Vehicles

Thus we have shown that by combining the measured properties of catalysts with the relevant engine emission data (exhaust gas

volume, composition, and temperature) it is possible to predict the emission control capabilities of commercially available units for specific applications. Honeycat Diesel Exhaust Purifiers are available in standard sizes (DEP 60, DEP 90, DEP 145) in which catalyst volumes are progressively increased. Choice of purifier will depend on both geometrical constraints for the particular engine installation and on the emission standards required. In general, it is convenient to use charts of the type shown in Fig. 6 to estimate the size of purifier required for the application under consideration. Most engines operate in the speed range shown on the shaded right-hand portion of the diagram and estimates of exhaust gas volume can be read directly on the y-axis for a given engine displacement size. By reference to the appropriate space velocity line, chosen on the basis of known performance and required emission target,

it is possible to choose the appropriate DEP. This is then installed on the automobile, fork lift truck or other equipment as near to the engine exhaust manifold as practicable.

Acknowledgement

The majority of results reported in this article were obtained during a Johnson Matthey research programme undertaken at Ricardo and Co. Engineers (1927) Ltd. Supplementary confirmatory data has been obtained during confidential projects in cooperation with various Johnson Matthey Chemicals Ltd. customers and with other research laboratories. The author wishes to thank the staff of Ricardo Ltd. for helpful discussions during the course of this work.

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Organometallic Chemistry of Platinum

ORGANOMETALLIC AND COORDINATION CHEMISTRY OF PLATINUM BY UMBERTO BELLUCO, Academic Press, London and New York, 1974, 701 pp. £17.50

This volume is a recent addition to the series of monographs on Organometallic Chemistry which includes P. M. Maitlis' "The Organic Chemistry of Palladium". It is the first book to be devoted entirely to the chemistry of platinum complexes and supplements F. R. Hartley's "The Chemistry of Platinum and Palladium".

Dr Belluco and his colleagues do not claim to have comprehensively covered the literature, especially in the section on coordination complexes. They have, however, provided the most up-to-date compilation of information necessary for a full appreciation of reactivity and bonding in the organometallic chemistry of platinum. A total of 1400 references, up to August 1973, are quoted in the text, in addition to a list of reviews on the subjects covered by each chapter.

The book opens with a chapter on coordination compounds which is sub-divided into the chemistry of platinum in its various oxidation states. Each section contains details of the physical and spectral properties of the relevant complexes. Specific descriptions of preparative methods have been omitted for the sake of brevity and the discussion is limited to general procedures and selected compounds. There is an additional section on oxidative addition to platinum(II) complexes.

There follows a discussion on the mechanism of substitution reactions with particular reference to the effect on reactivity of entering and leaving groups, *cis* and *trans* ligands, and the nature of the solvent.

There is also a very brief comparison with the reactivities found in other d^8 square planar systems.

The organometallic chemistry of the element is treated according to the nature of the ligands, with chapters on hydride complexes, metal-Group IV σ -bonded complexes, and compounds formed with unsaturated hydrocarbons. Each chapter is sub-divided as for the coordination compounds of a given oxidation state, but with particular emphasis on the preparative chemistry. In the five chapters on the complexes of platinum, extensive use has been made of tabulated nuclear magnetic resonance, infrared and Raman spectral data, and there are numerous illustrations of the molecular structures of significant complexes.

The final chapter is on homogeneous catalysis, where the emphasis is on the hydrogenation and isomerisation of olefins by platinum(II) complexes. However, the inclusion of short sections on homogeneous catalysis by other d^8 metal complexes appears rather incongruous when details of the industrially viable homogeneous hydrosilation catalyst, *trans*-Pt(Et₂S)₂Cl₂, have been omitted.

There is an adequate subject index, but the reviewer regrets the absence of author and formula indices which are found most useful in W. P. Griffith's "The Chemistry of the Rarer Platinum Metals".

Overall, the book is a welcome addition to the literature and will be valued by students and practical chemists alike.

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