Particulate Emissions from Vehicles

By

Peter Eastwood
Ford Motor Company, Ltd.

John Wiley & Sons, Ltd

Particulate Emissions from Vehicles

Wiley-Professional Engineering Publishing Series

This series of books from John Wiley Ltd and Professional Engineering Publishing Ltd aims to promote scientific and technical texts of exceptional academic quality that have a particular appeal to the professional engineer.

Forthcoming titles:

Vehicle Particulate Emissions
Peter Eastwood

Suspension Analysis and Computational Geometry
John C. Dixon

Managing Reliability Growth in Engineering Design: Decisions, Data and Modelling
Lesley Walls and John Quigley

Particulate Emissions from Vehicles

By

Peter Eastwood
Ford Motor Company, Ltd.

John Wiley & Sons, Ltd

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester,
West Sussex PO19 8SQ, England

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): cs-books@wiley.co.uk
Visit our Home Page on www.wiley.com

Other Wiley Editorial Offices

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 42 McDougall Street, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 6045 Freemont Blvd, Mississauga, ONT, L5R 4J3

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Library of Congress Cataloging in Publication Data

Eastwood, Peter, 1963–
  Particulate emissions from motor vehicles / Peter Eastwood.
    p. cm.
  Includes bibliographical references and index.
  ISBN 978-0-470-72455-2 (cloth)
  1. Automobiles—Motors—Exhaust gas. I. Title.
  TD886.5.E205 2008
  629.25′28—dc22   2007044839

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 978-0-470-72455-2

Typeset in 9/11pt Times by Integra Software Services Pvt. Ltd, Pondicherry, India
Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

Contents

Preface

One of my immediate colleagues once claimed, jokingly (I suppose), that my interest in exhaust gas is ‘obsessive and unnatural’. I do not, myself, see this as prurience, but, I suppose, a healthy interest in exhaust gas is reasonable enough for someone whose career has been associated, in one way or another, with motor vehicle pollution for nearly twenty years. Indeed, I don’t see that I would have remained in this field were it otherwise. At one time I may well have thought, with the presumption that so much characterises youth, that I would one day understand everything that is to be understood about this fascinating subject. But, even after having closely studied what must, by now, be many thousands of research papers, I still come across conjectures and abstruse speculations that are new to me.

Make no mistake; there is no shortage of intellectual sustenance to be had from the subject of particulate emissions from motor vehicles. Despite having received the attention of the ablest researchers for decades, there is still very, very much that is not understood. Perhaps we should remember to turn and look back occasionally, and remind ourselves of what has been learned, even in just the last decade: this is also very much. It was the avalanche of research papers beginning in the 1990s that, in fact, convinced me of the need to supply a coherent monograph in this field. True, there are already many excellent books on internal combustion engines, on polluting particles in the atmosphere, and on aerosol science and technology. My intention has been to supply a text in the region where these three fields intersect. Yes: exhaust gas is very much an aerosol, no matter how much this term may be associated with deodorants. Exhaust gas always carries particles of one sort or another.

The gestation of the present text has, regrettably, been a long one; and I blench at the thought that my first book, *Critical Topics in Exhaust Gas Aftertreatment*, was published no less than eight years ago. Tellingly, there is no suggestion here of prolific authorship. Well, art is long and life is short. But one reason for this delay is clear: an excess of zeal to include the latest research; and there were times when it seemed that papers were being published faster than I could review them. This is a vibrant field, if ever there was one.

Hence my regular consternation (nay, exasperation) with persons who say to me, occasionally, that my field is ‘specialist’ – usually with an accusing frown, as if I’m expected to bow my head in shame, having been ‘found out’. This reminds me of the scholastic debate about how many angels can dance on the head of a pin – used in modern times to parody esoteric and parochial academic research. Surely, the existence of many thousands of research papers in this field argues against parochialism. I look around my immediate workplace: no doubt more than half the people around me would have to seek employment elsewhere if the exhaust gas discharged into the atmosphere was of no importance in motor vehicle design and manufacture.

What distinguishes particulate emissions from other types of atmospheric pollutant is *visibility*; indeed, a high concentration of particles, emanating from some form of combustion process, is what we call ‘smoke’. This visibility ensures immediacy in the eyes of the public, for smoke provides the most obvious indication that some form of pollution is in progress. All (Western) industrial cities were once plagued by smogs generated by coal-burning; this air pollution is now lodged in our cultural psyche, indissolubly linked to London of the Victorian age. For example, contemporary costume dramas featuring Sir Arthur Conan Doyle's famous sleuth would be utterly unthinkable without some 'pea-souper' as a suitable backdrop. Alas, the particles we face today are quite different, as this text shows . . .

It is revealing to note that pollution by the traditional 'smokestack' industries has not always been censored. In former times people were well aware of the close association between industrial production and national prosperity – I'm thinking of advertising literature in previous decades. Then there is the association between industrial production and national security, as evidenced by 'home front' posters during the world wars. The complete absence of smoking factory chimneys in today's corporate advertising betrays this shifted emphasis.

Let us bring these sermonic musings to a close. Certain persons have been kind enough to offer their advice on sections of the draft manuscript, or to elucidate specific issues that to me remained stubbornly obscure: I wish therefore to acknowledge Nicos Ladommatos, Matti Maricq, Tony Collier, Khizer Tufail and Haiwen Song. Finally, I wish to thank my doctoral supervisor Timothy Claypole for his abiding advice – namely, that one should never apologise for doing a piece of good work – which proved invaluable to me in 1995.

Peter Eastwood
Dunton, 2007

Acronyms and Abbreviations

ACS	American Cancer Society
AFR	air–fuel ratio
ATDC	after top dead centre
BC	black carbon
BHM	binary homogeneous nucleation
BMEP	brake mean effective pressure
BS	black smoke
BTDC	before top dead centre
CA	crank angle
CAD	crank angle degrees
CARB	California Air Resources Board
CNC	condensation nuclei counter
CNG	compressed natural gas
CNN	cloud condensation nuclei
CO	carbon monoxide
COPD	chronic obstructive pulmonary disease
CSHVR	city–suburban heavy vehicle route
CVS	constant-volume sampling
DEE	diethyl ether
DEP	diesel engine particulate
DI	direct injection
DIA	digital-imaging algorithms
DISI	direct-injection spark ignition
DMA	differential mobility analyser
DMC	dimethoxycarbonate
DME	dimethyl ether
DMM	dimethoxymethane
DMPS	differential mobility particle sizer
DNA	deoxyribonucleic acid
DPF	diesel particulate filter
EAA	electrical aerosol analyser
EC	elemental carbon

ELPI	electrical low-pressure impactor
EOI	end of injection
EPA	Environmental Protection Agency
ESC	European steady-state cycle
ETC	European transient cycle
EUDC	extra-urban drive cycle
FAME	fatty acid methyl ester
FBC	fuel-borne catalyst
FEV	forced expired volume
FID	flame ionisation detector
FIE	fuel injection equipment
FTP	Federal Test Procedure
FVC	forced vital capacity
GC	gas chromatograph(y)
GDI	gasoline direct injection
GEP	gasoline engine particulate
HACA	hydrogen abstraction and acetylene addition
HC	hydrocarbons (particularly those that are gases at $>190\,^{\circ}\mathrm{C}$)
HCCI	homogeneous charge compression ignition
HWFET	highway fuel economy test
IDI	indirect injection
IFN	ice-forming nuclei
IM240	Inspection and Maintenance (240)
IMEP	indicated mean effective pressure
IMN	ion-mediated nucleation
ISO	International Organization for Standardization
LES	laser elastic scattering
LII	laser-induced incandescence
LMMS	laser microprobe mass spectrometry
LPG	liquefied petroleum gas
MAF	mass air flow (sensor)
MATES	Multiple Air Toxics Exposure Study
MOUDI	micro-orifice uniform deposit impactor
MPI	multi-point injection
MS	mass spectrometry
MTBE	methyl t-butyl ether
NA	naturally aspirated
NAAQS	National Ambient Air Quality Standards (USA)
NEDC	New European Driving Cycle
NIEHS	National Institute for Environmental Health Sciences (US)
NIOSH	National Institute for Occupational Health (US)
NMMAPS	National Morbidity, Mortality and Air Pollution Study
NO_x	oxides of nitrogen
NPAH	nitro-PAH
OC	organic carbon
OFR	oil–fuel ratio
PAH	polycyclic aromatic hydrocarbon(s)
PCDD	polychlorinated dibenzo-*p*-dioxins

PCDF	polychlorinated dibenzofurans
PCI	premixed compression ignition
PCV	positive crankcase ventilation
PMN	polymorphonuclear neutrophil leukocytes
PPCI	partially premixed compression ignition
PGM	platinum group metals
PM	particulate matter
QCM	quartz crystal microbalance
REE	rapeseed ethyl ester
RME	rapeseed methyl ester
ROFA	residual oil fly ash
RON	research octane number
ROS	reactive oxygen species
SBR	styrene–butadiene rubber
SME	soya methyl ester
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
SOC	secondary organic carbon (particles)
SOF	soluble organic fraction
SOI	start of injection
TC	turbocharged
TDC	top dead centre
TEL	tetraethyl lead
TEOM	tapered-element oscillating microbalance
TGA	thermal gravimetric analysis
TSP	total suspended particles
UDC	urban drive cycle
VCO	valve-covered orifice
VGT	variable-geometry turbine
VOF	volatile organic fraction
WHO	World Health Organization
WMTC	World Motor Cycle Test Cycle
WOT	wide-open throttle
XOC	XAD-2 resin organic component (i.e. vapour-phase organics)

About the Author

Dr. Eastwood graduated from University College, Swansea, UK, in 1985, with a B.Sc. in Mechanical Engineering; followed in 1992 by a Ph.D. in Mechanical and Electrical Engineering, with a thesis entitled *Exhaust Gas Sensors for Engine Management*. There followed a post as Royal Society Post-Doctoral Research Fellow at the Institute for Physical and Theoretical Chemistry, Tübingen, Germany, then under the direction of Prof. Dr. W. Göpel. Since then Dr. Eastwood has worked in industry in a variety of research and development roles, all of them associated in one way or another with the technology of motor vehicle pollution control. His monograph, *Critical Topics in Exhaust Gas Aftertreatment*, was published by Research Studies Press in 2000.

1

Introduction

The first trade-off between *utility* and *amenity* probably arose with fire. The utility was manifold: cooking, heating and illumination; and also artwork, as facilitated by a mysterious black pigment: ancient hands, pressed against cave walls, and exposed to strongly sooting flames, have left their silhouettes for modernity. The luminosity of the fire, and to some extent the heat, stemmed from the black pigment – namely, *soot*. Yet the amenity was also degraded, as the soot particles, when inhaled, were prejudicial to health; and it was fire, perhaps, that engendered the first respiratory diseases. Such ailments still plague developing countries, where households continue to rely on a variety of stoves for cooking and heating, ventilation for which is poor or virtually nonexistent (Koshland and Fischer, 2002).[1]

Smoke became more inimical once population densities increased to those of the first civilisations, and the problem greatly accelerated once coal began to replace wood as the principal fuel (Brimblecombe, 2001). The great forests of England were swiftly dwindling before a rapidly expanding population: fuel was needed for energy, and land for agriculture. The competition, between utility and amenity, is written into the legislative record: Edward I (reigned 1272–1307) issued a royal proclamation forbidding coal-burning in London; Edward II (reigned 1307–1327) ordered the torture of persons fouling the air with coal smoke; Richard II (reigned 1377–1399), more humanely, chose to control coal-burning via taxation; Henry V (reigned 1413–1422) established a commission to regulate the entry of coal into London (Wilson R., 1996); and Elizabeth I (reigned 1558–1603) legislated against coal-burning whenever Parliament was sitting.

---

[1] Some misguided souls in the developed world express a preference for the ‘naturalness’ of open fires. This position is untenable even from the environmental standpoint that such people profess to adopt. Open fires are inefficient and largely uncontrolled; they consequently release into the atmosphere large quantities of soot and sundry organic compounds – with genuine toxicological risks. Contrastingly, the combustion inside today’s engines is controlled to great precision; the pollution is excessive because motor vehicles are present at high density, not because they are particularly polluting on a unit basis.

Particulate Emissions from Vehicles P. Eastwood

In 1648, coughing Londoners petitioned the government to prohibit the importation of coal from Newcastle, citing the injurious effects of the smoke; but they were unsuccessful. And in 1661, the famous diarist John Evelyn wrote:

> It is this horrid smoake, which obscures our churches and makes our palaces look old, which fouls our clothes and corrupts the waters so that the very rain and refreshing dews which fall in the several seasons precipitate this impure vapour, which with its black and tenacious quality, spots and contaminates whatever is exposed to it. (Cited by Wilson R., 1996).

What provided the greatest impetus of all was the Industrial Revolution: by 1819, the problem had become so conspicuous that Parliament appointed a committee to investigate how to make steam engines and furnaces less prejudicial to public health. It was concluded that smoke could be effectively controlled . . . but no action was taken. As a question of social policy, addressing smoke was often viewed as prejudicial to the nation's economy, and public good was held more important than private need. There also seems to have been a subtle transition from regulation as 'nuisance' to regulation as 'negligence' (Farrell and Keating, 2000). A technical question was whether to prevent the formation of smoke in the first place; whether the smoke, once formed, should be collected prior to emission; or whether the smoke, once emitted, should be more effectively dispersed, under the time-honoured cynicism 'the solution to pollution is dilution'. The construction of ever-higher chimney stacks, as the Industrial Revolution advanced, bears testimony to the dispersion principle (and in the modern era, power stations send their pollution above the inversion layer).

Smoke emissions from locomotives were finally regulated by the Railway Clauses Act of 1845, and from factory furnaces by the Town Improvement Clauses Act of 1847. From 1875, English law regulated smoke from factory chimneys under clauses in the Public Health Acts; London was singled out for more severe restrictions. This legislation was subsequently modified by the Smoke Abatement Act of 1926, which invested local authorities with powers to enforce the provision of equipment in new buildings as might prevent smoke. (Domestic grates were not, however, included.) Several towns established 'smokeless zones', wherein all smoke emissions were prohibited (Fishenden, 1964).

These measures were insufficient. In the 1950s, the duration of sunshine in cities such as Leeds, Sheffield and Manchester, during the winter months (when domestic hearths saw most use), was less than half that in the outlying districts. Pea-soup smogs, or just 'pea-soupers', sometimes lasting for several days, plagued many cities, and (quite apart from respiratory ailments) were responsible for numerous road accidents. As recently as 1950 it was reported that, in Glasgow, three tonnes of soot fell to earth per acre per year (cited by Wilson R., 1996).

The incident which undoubtedly provided the greatest case for further legislation was the notorious London smog of December 4–9, 1952, which arose through a freak combination of low wind speed, temperature inversion and dry weather; local levels of atmospheric particulate peaked at $7\,\mathrm{mg/m^3}$ (Maynard, 2001) – ten times the amount normally seen to day, even in the most heavily polluted of cities. The smog is reputed to have killed 4000 people:[2] the association between mortality, smoke and sulphur dioxide (SO_2) is pointedly illustrated by Figure 1.1 (cited by Wilson R., 1996). During this event, deaths attributed to bronchitis and pneumonia increased eightfold and threefold, respectively; there were also increases in deaths attributed to other respiratory or cardiac diseases (Higgins I.T.T.,

---

[2] This incident is wearisomely related in virtually every book on air pollution, amongst which the present one is no exception. Around 4000 deaths is the figure usually quoted. Recent research reported in the *Daily Telegraph*, Dec. 14, 2002, suggests the smog-related deaths to have been confused with those of a flu epidemic, and that the real figure could be as high as 12 000. The newspaper article credits this work to D. Davis and M. Bell, but the present author has been unable to locate any further information.

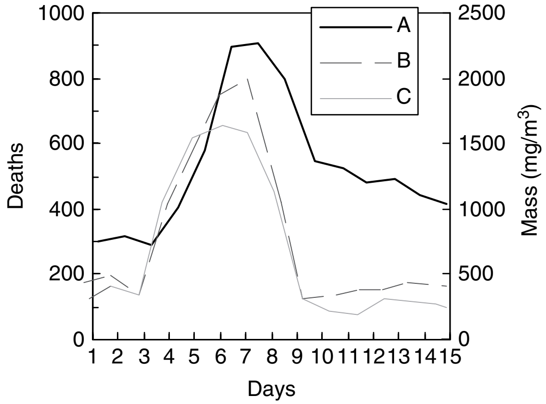

Figure 1.1 The London smog of December, 1952, and its fatal effects: A, number of deaths; B, mass concentration of SO_2; C, mass concentration of smoke. The graph is taken from Wilson R. (1996) (original reference Beaver (1953)). (The concentrations are averages over several sites).

1971). But post-mortems failed to reveal anything specifically particle-related; the common feature was that persons with cardio-respiratory diseases suffered exacerbations of their symptoms, and that some died as a result (Maynard, 2001). Morbidity rates increased also, as seen in various statistics for hospitalisations and sickness-benefit payments.

Suitably chastened, Parliament introduced the Clean Air Act of 1956, making the emission of dark smoke an offence. But mortality and morbidity in London, for certain respiratory diseases, remained until the early 1960s fairly well correlated with smoke and SO_2. After this period the proscription of smoke seems finally to have taken effect, inasmuch as mass concentrations fell from 300 to $60\,\mu g/m^3$; and there is some evidence of a concomitant improvement in public health (studies cited by Higgins I.T.T., 1971).

To be sure, the reason for the demise of pea-soup smogs was widespread conversion of domestic heating appliances to natural gas (Farrell and Keating, 2000). (The dieselisation of railways and small-scale power generation was another factor.) Smoke is a key symptom of poor air–fuel mixing: an inability to supply sufficient oxygen to the primary combustion zone is the eternal problem with solid fuels. And in the domestic arena, coal was often burned in a haphazard and uncontrolled way. Natural gas can be mixed with air automatically and far more precisely; hence the cleanliness of the combustion becomes far less dependent on the competence, or diligence, of the user.

Natural gas possesses two other advantages – it is low in sulphur and incombustible ash (principally metals). In the presence of moisture, and the catalytic effects of incombustible metals emitted as ‘fly ash’, fuel sulphur invariably finishes up in the atmosphere as *sulphuric acid*. The combination of soot, ash and acid was what formed the infamous smogs. This drives home forcefully the importance of *secondary* pollution: not directly emitted, but formed subsequently through ongoing atmospheric reactions. Secondary pollution greatly obfuscates the protection of ambient air quality: it can only be controlled indirectly, via the primary pollution, and a thorough knowledge of atmospheric processes.

We have followed the history of smoke, from the first beginnings to the modern era; and from primeval man, to the grimy image, etched into our cultural psyche, of the nineteenth-century industrial city. But how does this relate to particles emitted by today’s internal combustion engines? This question does not, usually, concern aesthetics, as exhaust plumes are less visible, indeed approaching invisibility, just as their offending dirt and filth are evanescent. Nor is the danger nowadays a slow asphyxiation by acrid smoke, because particle concentrations in the ambient atmosphere are much lower than in the instances described – by two orders of magnitude. It should be emphasised that the pollution in the aforementioned London smog episode provided evidence of the risks to public health – evidence that was unambiguous and unmistakable. The situation today is not nearly so clear-cut; and considerably greater efforts are needed to avoid poorly focused or ineffective legislation (Hall *et al.*, 1998).

1.1 Air Traffic

Emissions legislation, directed at aircraft, began to appear at around the same time as for motor vehicles, i.e. in the 1960s (Kittredge and NcNutt, 1971). This is not exactly a coincidence: there is to some extent a parallel between the two types of transport: similar pollutants are emitted (carbon monoxide, oxides of nitrogen, particulate and hydrocarbons), and levels of traffic increased rapidly at about the same time. But in aviation, the internal combustion engine was not the culprit. The need to control emissions, especially those of smoke, first arose towards the end of the 1950s, when the gas turbine began to replace the internal combustion engine as the preferred power plant. This was not only a problem with civilian airliners: the conspicuousness of the trails was particularly undesirable with military aircraft (Fiorello, 1968).

In fact, the earliest jets did not smoke appreciably; the problem seems to have been instigated by increases in combustion pressure and heat release rates, undertaken to improve performance (Shayeson, 1967). Smoke emitted by aircraft was particularly noticeable during take-off and on the final approach to landing. The sight and sound of jet aircraft, especially when on full thrust, further focused attention; and an aircraft's smoke trail is inherently visible against an empty sky, unlike on the ground, where neighbouring buildings render assistance in hiding the evidence (Parker, 1971).

In gas turbines, soot is formed in fuel-rich regions of the combustor; it can be burned up prior to emission, but this action is impeded by overly rapid quenching. To combat soot, therefore, the engine manufacturers were forced to redesign their combustors, as, unlike with motor vehicles, aftertreatment, that is, an exhaust gas clean-up, is impractical (Nelson, 1974). It was, apparently, possible to control the soot by directing air into the primary combustion zone, without, moreover, unacceptable increases in NO_x (Bristol, 1971). This soot–NO_x trade-off–since *both* pollutants must be reduced–is a constraint that continues up to the present time (Gupta A.K., 1997). The same trade-off is inherent in the diesel engine (to which we shall shortly turn): this is the principal reason why diesel soot has proven so intractable.

1.2 Motor Vehicles

Smoke has always been emitted by motor vehicles; and its sheer visibility, competing with the malodorous emission, ensures immediacy in the eyes, and noses, of the public. Yet in the days of Otto and Diesel, gasoline engines were denounced just as much as diesel engines. There is an interesting paper published by the newly formed US Society of Automobile Engineers [*sic*], from before the First World War, which castigates automobiles of 'the early days' [*sic*] as 'ill-smelling affairs' (Howe, 1910). It was at this time that New York City's Department of Health extended an old smoke ordinance to include motor vehicles: 'No person shall cause, suffer or allow dense smoke to be discharged from any building, vessel, stationary or locomotive engine or motor vehicle, place or premises within the City of New York.' Intriguingly, the ordinance gave no definition for a smoke density that *was* acceptable, even though it did, apparently, make a culprit liable to police arrest. (Perhaps the authorities realised just how difficult meaningful measurements of smoke are to conduct.) The author of the paper recognises the close association between smoke and tampering, and calls for manufacturers to prohibit maladjustment of carburettors such that black smoke is emitted. Apparently, it was not unknown for exhaust gas at this time to contain carbon monoxide to the tune of 12 % [*sic*].

The introduction of leaded gasoline in the 1920s gave rise to a new type of particulate emission. Tetraethyl lead was added to gasoline as an antiknock agent; and, to prevent the formation of lead deposits in the engine, ethylene dichloride and dibromide, as scavenging agents, were also added. These additives were emitted as particles of lead bromochloride, bromide and chloride. Because they were invisible, lead particles were arguably more insidious than smoke. But no changes were made until motor vehicle ownership reached modern-day proportions.

The eventual withdrawal of leaded gasoline happened for two cogent reasons. First, elevated levels of lead were discovered in the blood of persons exposed to traffic emissions. This raised a host of health issues (Russell Jones, 1987), a chief one being the suspected impairment of child development. Second, a pressing need had arisen to tackle other emissions, and catalytic converters were the only feasible technology with which to do this. Catalysts are swiftly poisoned by lead, and no aftertreatment sufficiently tolerant to this metal has ever been found.

The USA in the 1970s saw the introduction of the first catalytic converters; they were for oxidation purposes only (unlike today's three-way catalysts). Perversely, this led to another type of particulate emission: droplets of sulphuric acid. Reading the literature with the benefit of hindsight, this problem appears to have come as something of a surprise to the automotive industry; however, the appearance of sulphuric acid, after burning fuel which contains trace amounts of sulphur, and passing the exhaust gas over an oxidising catalyst, will not come as a surprise to any chemist. Again, this problem was not really solved as such; rather, technology simply moved in another direction. The introduction of three-way catalysts in the 1980s forced the adoption of stoichiometric, rather than lean air–fuel ratios; and the oxidising conditions in the exhaust necessary for the formation of sulphuric acid were lost.

Thus far we have discussed particles that are, in a sense, interlopers, inasmuch as they arise by side reactions in the combustion process. Not all particles are produced this way. Unburned fuel, if emitted in sufficiently large quantities, forms liquid droplets in the exhaust plume, and these droplets are perceived as *white* smoke. For engines that have been designed successfully, calibrated competently and maintained assiduously, this type of smoke is not an issue. Emissions legislation now places strict limits on the quantity of unburned hydrocarbons that may be emitted; and to obtain white smoke, these limits must be exceeded by an order of magnitude, so that this phenomenon is a little academic. White smoke may still be a problem, however, during cold starts, especially at low ambient temperatures. Similarly, *blue* smoke, if caused by the escape of lubricating oil, is indicative of improper or inadequate maintenance, and seldom otherwise seen.

Finally, there is the long-standing issue of *black* smoke, chiefly discharged by diesel engines, and whose characteristic blackness arises from the element carbon. Black smoke appears to be an unfortunate and ineluctable consequence of diesel combustion, if only because it has frustrated the attempts of generations of engineers to eliminate it. Solely from an engine performance perspective, black smoke reflects the efficiency, or perhaps more appropriately, the inefficiency of the combustion, because it represents lost energy. But that is not quite the point: with today's diesel engines, the carbon that is usually emitted as soot, if it were to be successfully burned, would make little difference to the overall combustion efficiency, whereas if a diesel engine at full load were to emit only 0.5 % of the fuel as black smoke, the result would be completely unacceptable from an emissions perspective. The combustion efficiency, taking into account unburned hydrocarbons, carbon monoxide and soot, is usually better than 98 %, so that, from an energy conversion perspective, the combustion is virtually complete (Heywood, 1988, p. 509). The implications for public health are a completely different issue.

1.3 The Legislative Framework

Up to now, ‘smoke’ and ‘particulate’ have been employed fairly loosely and interchangeably. From now on this practice will be insufficient, and both terms must be defined much more closely. Strictly speaking, ‘smoke’ denotes an *aerosol*, i.e. a suspension of particles in a gas, whereas ‘particulate’ describes a collection of these particles, say, on a filter.[3] But, passing from these semantic quibbles, a more important difference, of a technical (and indeed environmental) nature, arises: when there is smoke, the presence of particles may be safely inferred; but when there are particles, these are not necessarily manifested as smoke. *Smoke, then, is the visible corollary of particulate*. Thus, ‘particulate’ is a considerably *broader* and indeed *all-encompassing* term: it incorporates smoke, and much else besides. So, we can now state this distinction explicitly, as follows:

- *Particulate.* All material which deposits on a filter.
- *Smoke.* All material which attenuates a beam of light.

These two definitions – both of which, incidentally, exclude condensed water – should not be confused: they are often directionally consistent, but this consistency is not by any means an essential prerequisite: in fact, the mass of particulate discharged by a smoking vehicle might actually be less than for a nonsmoking vehicle (Knapp *et al.*, 2003). This is because particle masses and particle interactions with light are entirely different measures – consistent only when the particles under investigation (size and composition) are also consistent.

In the USA, smoke from heavy-duty diesels was first legislated on in 1970 as ‘opacity’, that is, the fraction of light successfully traversing the exhaust stream. The development of particulate-control legislation is complicated (e.g. Cucchi and Hublin, 1989; Walsh and Bradow, 1991; Walsh, 1993; Charmley, 2004), but, simplifying somewhat, the first diesel particulate standards in the world were established in the USA in 1980, and related to passenger cars and light-duty trucks; heavy-duty engines and trucks were subsequently covered in 1985. In Europe, particulate emissions from diesel engines were first controlled in 1989, via EC Directives 88/436, 91/441 and 91/542 (Hall *et al.*, 1998).

Particulate is now strictly regulated in most countries, and the mass emitted by both light-duty (g/km) and heavy-duty (g/kW h) diesels has decreased since the 1970s, by more than two orders of magnitude. It is not improper to observe that the debate between industry and legislatures about these regulations has been contentious at times (Merrion, 2003). While the enactment of this legislation has undoubtedly helped to shape, and propel forward, the technology of emission control, the diesel engine has, at times, seemed threatened with extinction (Pethers, 1998); indeed, the downward trend in statutory requirements is set to continue unabated.

Current legislative practice in most countries extends, in a belt-and-braces manner, to smoke *and* particulate. But since smoke is far more conveniently measured, it tends to be used as an in-use compliance test, i.e. for *individual* vehicles during the course of their lives – perhaps those pulled over by the authorities for roadside checks. In the UK it is an offence for any vehicle to emit smoke at levels that impair visibility for other drivers; clearly, therefore, this is not so much to protect air quality as to ensure road safety. Smoke is assessed by a roadside or garage test, in which the clutch is disengaged and the engine rapidly accelerated up to the governor run-out (on passenger cars, usually between 4000 and 5000 rpm). This is the so-called ‘free acceleration’ test. It is quick and convenient, but says nothing about the smoke emitted during *real* driving, i.e. with the engine operated over a

---

[3] Exact speakers of English prefer to stay with this strict definition; but in this text, ‘particulate’ is applied more loosely insofar as it denotes also the suspended particles *prior* to collection.

genuine duty cycle. The free acceleration test is the sum total of what a vehicle is likely to experience after it has been sold, according to the current regulations.

The regulations to be satisfied *before* sale relate to a vehicle *model*, and are known as ‘type approval’ or ‘homologation’. These regulations are much stricter, and the manufacturer must demonstrate satisfactory levels of smoke *and* particulate. On an engine dynamometer, the smoke is assessed in two ways: first, for a progressive series of steady states along the full load curve (otherwise known as the torque limit), and second, for a free acceleration test as already described. Particulate emissions from an actual vehicle (i.e. the full power train) are assessed on a chassis dynamometer.[4] The vehicle is run over a (transient) drive cycle, during which the exhaust gas is fed into a ‘dilution tunnel’, mixed with air, and then filtered. This procedure is designed, among other things, to approximate the dilution of real exhaust plumes in the ambient. Current legislation mandates a dilution such that the exhaust gas temperature at the filter is less than or equal to 52°C:[5] this condition is pivotal, as it decides the transfer of material from the gas phase into the particulate phase. Once the drive cycle is completed, the filter is removed, conditioned to a certain temperature and humidity, and then, to determine the mass of particulate it has retained, simply weighed.

---

[4] This description focuses on light-duty vehicles. Legislative practice for heavy-duty vehicles is different; engine dynamometer rather than chassis dynamometer tests are preferred. Some countries also only use steady-state (cruise) tests. Test protocols vary considerably from country to country, and are continually evolving; the information here is necessarily generalised.

[5] This is the long-standing specification, the laxity of which in view of today’s stringent emission control legislation is well recognised. At the time of writing, tighter specifications such as 47 ± 5°C are under discussion (Wu *et al.*, 2007).

2

Fundamentals

2.1 Introduction

The present chapter is divided into three main sections. The first describes the physics, and to a lesser extent the chemistry, of particles when suspended in a gas: what has become known as 'aerosol science'. The physicochemical mechanisms in operation, from one aerosol to another, greatly depend on particle *size*. We look at the various forces that determine particle motion, or *transport*, and then turn to *mutability*, which simply means that particles are constantly changing in shape and form.

The second section, on atmospheric particles, is included in order to place motor vehicle particulate in an appropriate context. The atmosphere is not simply 79 parts nitrogen and 21 parts oxygen, with trace quantities of other gases. Such a description, although convenient, grossly overlooks a component of profound and ubiquitous influence; for the atmosphere is, in fact, thronging with innumerable particles; and this makes it not so much a gas, as a *multiphase system*. This particle soup, the 'atmospheric aerosol', is of mind-boggling complexity.

In the third section, we begin our study of the particulate actually discharged by motor vehicles. Knowledge in this area is gained, principally, by passing the exhaust gas, perhaps in raw, but more usually in diluted, form through a filter, and studying the particulate trapped thereon. The material caught this way is astonishingly diverse. The final point addressed is whether one should consider the *number* of particles or the *mass* of particles. The implications of this decision loom large in contemporary emission control.

2.2 Properties of Aerosol Particles

An immensely helpful feature of the word 'particle' is that it encompasses, without distinguishing, the liquid and solid phases of matter; indeed, this collective grouping conveniently signifies a *third* state, the 'particulate phase' – an umbrella term that will be much used in this text. But, this said, it is equally important to understand that the liquid and solid states appertain to the *macroscopic* world,

---

Particulate Emissions from Vehicles P. Eastwood

i.e. when material is present in bulk. Intuitively, the physics and chemistry of the bulk cannot continue to apply no matter how finely divided the material; and this is indeed the case.

Aerosol science is a distinct scientific discipline in its own right (Spurny, 2000f), the emergence of which is fairly recent in the scientific lineage; indeed, 'aerosol' seems to have been coined in the early 1920s, although many of the important fundamental observations date from the Victorian era. A wide range of subdisciplines, and an incomprehensibly wide range of aerosols, are encompassed. To the general public, aerosols are hairsprays, deodorants and the like; but to the technologist, any collection of particles suspended in a gas is an aerosol.[1] Hence aerosols are, by their very nature, *multiphase* systems. They can be formed in numerous ways: the disintegration of liquids and solids, the resuspension of deposited particles, the break-up of agglomerated particles, and the condensation of gases into particles.

Aerosols are impermanent and highly dynamic, because their constituent particles are notoriously and capriciously protean. Interactions between particles, between particles and the gas molecules that surround them, and between particles and the solid walls that contain them are unending. Particle properties cannot, for this reason, be divorced from the conditions to which an aerosol is subjected. Heating, cooling, dilution, residence time and the like all potentially influence particle size and composition – and generally do. If not properly controlled, many of the processes outlined below give rise to variable, unpredictable or even bogus results. The paramountcy of this remark cannot be overstated.

2.2.1 Diameter and Shape

Aerosol science is fundamentally predicated on one parameter: particle *size*. But so characterising particles is problematical for various reasons. Excepting, for example, the case of liquid droplets, which offer the convenience of sphericity, irregular morphologies are the rule rather than the exception. Of course, such irregularity need not be a problem if particles of different sizes are *geometrically similar*, as one characteristic dimension may then be arbitrarily selected; but, again, in practice this condition is seldom the case. Consequently, there have arisen in aerosol science various ways by which to define particle size. This is inconvenient because the various definitions cannot always be easily interrelated. And although in aerosol science it is common to speak of a 'diameter', as of a sphere, this term requires some elucidation, as it does not refer, to any geometrical dimension that could be verified directly, as under a microscope: the suggestion of circularity should not, therefore, be taken literally.

Various definitions are based on geometry (Mark, 1998). We may, for instance, consider a spherical particle of *equivalent* surface area or volume; this is referred to as a 'fundamental' diameter. Equally, we may allow the particle to cast its shadow onto a background, and then calculate the perimeter or surface area of the shadow, referring this back to an equivalent spherical particle; this is the 'projected' diameter. The greatest possible distance between two parallel lines tangent to the particle profile is 'Feret's diameter'. Obviously, there are many possibilities.

The ponderous nature of visual or optical assessments cannot be gainsaid. And although this ponderousness is indubitably lightened by the advent of computer imaging and automated imaging processing, there seems little likelihood of real-time measurements. In any case, there is always the variability inherent in particle orientation.

Practical particle-sizing instruments do not report diameters based on, or even derived from, direct geometrical assessments. These instruments exploit the fact that particles respond to certain forces in

---

[1] Similarly, a suspension of particles in a liquid is referred to as a 'colloid'. Many of the theoretical principles for colloids are the same as for aerosols, but, with the exception of soot in oil (Section 6.3), in this work we are concerned only with the latter.