Fuel additives and the environment

Acknowledgement

This is the second edition of a paper based upon the work of a special task force of the ATC (the Technical Committee of Petroleum Additive Manufacturers in Europe), established to bring together existing information on the effects and impacts of fuel additives and to use that information to put into perspective the benefits to man and the environment provided by fuel additive technology. New information for the second edition was provided by members of the Fuel Additives Group (K Barnes, WD Byfleet, S King, H Mach, NJ Tilling, T Russell, HP Sengers).

1. Preface to the Second Edition

In 1993 the ATC (the Technical Committee of Petroleum Additive Manufacturers in Europe) published a paper entitled "Lubricant Additives and the Environment"(1). The objective of that paper was to inform government regulators and others about our industry, and in particular about the impact of lubricant additives on the environment. The paper was first presented at the CEC Symposium in Birmingham in May 1993, and several hundred copies have since been distributed and well received throughout Europe.

The success of that paper showed up the need to produce a companion publication on Fuel Additives and that was duly published in 1994 as ATC Document 52. Since that time there has been major EU legislation on automotive emissions and fuel qualities which took effect in 1996 and 2000 and which will also apply in 2005. A direct effect of this legislation has been to eliminate almost entirely the large market for lead anti-knock additives. An indirect effect has been to stimulate new markets for lead replacement additives in gasoline and lubricity additives in diesel fuel. The automotive industry's move to fuel injectors from carburettors has all but eliminated the market for carburettor cleanliness additives. This publication's original "fate analysis" of fuel additives based on 1992 vehicle emissions legislation is now clearly obsolete. All these and other factors have encouraged ATC to publish a revised edition of that publication, with updated data but maintaining the original publication objectives.

The presentation confines itself to a study of fuel additives as used in automotive gasoline and diesel fuels, within the 19 countries of OECD Europe - Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, Turkey and U.K. It discusses their chemistry and use, the benefits they provide and their fate in the environment. The work is based on a wide range of published data, and these references are shown in the bibliography in Appendix A.

The reader should be aware, however, of some fuel products which are not covered:

(i) With oxygenates (alcohols and MTBE/ ETBE) increasingly added to gasoline, they are often thought of as additives: they are not, however, the performance-enhancing chemicals which are the subject of this paper, neither are they sold by nor the concern of ATC member companies.

(ii) Lead additives are part of the history of the fuel additives industry but have never fallen within the direct remit of ATC. Since 2000 there have been essentially no sales of lead additives in the EU. Readers seeking information on these additives should contact the manufacturers directly.

(iii) Secondary (or after treatment) fuel additives are sold in the retail market in small packages. ATC member companies, however, do not sell these products directly and these are also not covered by this paper.

(iv) Fuel additives sold for use in domestic and industrial heating oils are not included, although the chemistries are sometimes similar to those used for diesel fuel additives.

2. The industry

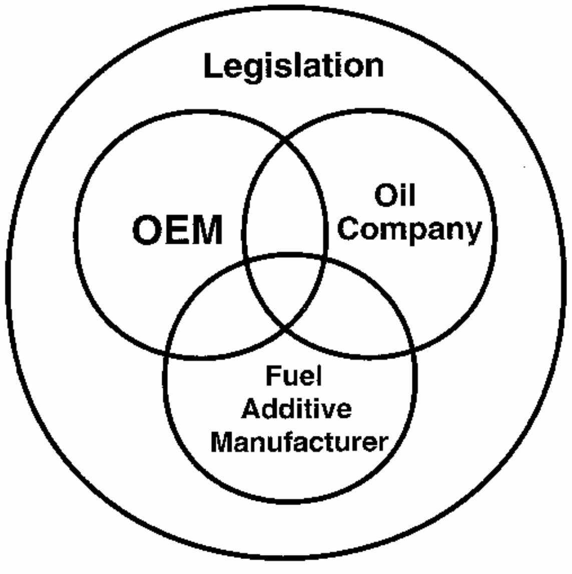
The previous paper discussed the organisation and objectives of the ATC, and it is not intended to repeat this. However, it is worth reiterating that the petroleum additives industry is research and development intensive, with the more important features being:

- world-wide expenditure on research and development around 500-600 million Euro per annum
- world-wide turnover around 12 times greater, with about one-third or 2,000 million Euro per annum in Europe
- about 3500 people employed direct in OECD Europe
- around 25 research and development and manufacturing sites in Europe, with the petroleum additives industry in Europe being a major exporter.

Its products are marketed solely to industrial users, and the customers are a wide range of fuel companies within the oil industry: it is the satisfaction of their needs which is its primary mission. It must also, however, be very sensitive to the needs of the motor industry or original equipment manufacturers (OEMs). As new challenges face vehicle and engine builders, they look to the suppliers of fuels (and functional fluids) for help. A good understanding of motor industry needs is essential if the additives industry is to plan and prioritise its research effort effectively.

Increasingly a fourth element is joining the traditional tripartite relationship between fuel, motor and additive industries. Environmental concerns and legislation are having an ever greater influence on product marketing for both the fuel and motor industries. The meeting, and indeed beating, of environmental targets and challenges is also a prime concern of the petroleum additives industry. Indeed, ATC would argue that many of today's environmental targets, e.g. continually reducing regulated emissions levels, can only be met with the help of appropriate additive technology. And just as the additives industry must maintain a dialogue with industry partners, it must also establish and maintain one with the regulators the better to understand their concerns and address their demands.

Figure 1 The importance of partnership



As part of its research, ATC has attempted to establish the size of the petroleum additives market in Europe. Some of the difficulties involved and the lack of public data sources are elaborated in the earlier paper "Lubricant Additives and the Environment" (1). The problems of establishing hard data for fuel additives are even greater. Nonetheless, starting from published figures(2) and updated by more recent information, ATC has established order of magnitude figures, in the belief that these do help to define the scope of the industry and are accurate enough to form the basis for meaningful conclusions. These are given in Figure 2. ATC is more than happy to discuss these with interested parties, and is prepared to consider modifying or refining them as appropriate.

Figure 2 Additive use in Europe - 1998

Product	**Tonnes**	**Comment**
Gasoline additives		
Deposit control additives	69,650	Estimated that 75% of European gasoline is treated with such packages.
Comprising:- detergent	30,500	
carrier fluid	23,350	
other	13,800	
Lead antiknock additives	11,250	Now almost zero. Use in EU banned since 2000 except for special cases.
Anti-Valve seat recession additives	2900	It was anticipated in 1998 that sales would increase in 2000 and that such products would be used in 2% of gasoline for a period of 2-5 years.
Sub-total	83,800	
Diesel additives		
Cetane improvers	19,850	Both refinery and package applications
Injector detergent packages	25,650	
Comprising: detergent	7,850	
antifoam	200	
other	17,600	
Lubricity improvers	5,250	Growth in use following the introduction of low sulphur specifications
Low temperature flow improvers	29,350	Used widely in winter months. In summer either not used or used at lower concentrations.

Sub-total	80,100	
Other Fuel Additives		
Antioxidants	2200	Aviation gasoline and kerosene
Antistatic additives	50	Limited very cold weather use in gasolines and more widespread use in low sulphur diesel
Corrosion inhibitors	1250	
Dehazers	2550	Linked to deposit control additive
Drag reducing agents	<100	Limited pipeline use
Dyes	350	Gasoline and diesel
Stability improvers	200	Primarily diesel
Reodourants	50	Primarily diesel
Metal deactivators	200	Mainly used in aviation gasoline and kerosene
Sub-total	6,850	
Total	170,750	

For the benefit of the reader, fuel additives have been subdivided into two main groups - gasoline and diesel fuel additives. They may also be considered in a different way as “distribution” or “vehicle fuel system” additives.

Distribution system additives are put into the fuel at a refinery and in general are used to help the refiner provide fuel which meets an internal or external specification at optimum cost. They will usually demonstrate their benefits in the distribution system, although some additives such as diesel fuel flow improvers will show benefits in the vehicle as well. Some of these additives may enhance the properties of the base fuel (e.g. corrosion inhibitors); some may help to maintain them (e.g. antioxidants, stabilizers). Others may aid the movement of fuel through the distribution chain and into the vehicle tank (e.g. pipeline drag reducers, demulsifiers, antifoams) or may be added for legal reasons (e.g. dyes and markers).

Vehicle fuel system additives, on the other hand, only begin to provide benefits when the fuel enters the engine inlet system or combustion chamber. They are sometimes added to the fuel at the refinery but more usually at a marketing terminal. Such additives are more likely to be specific or proprietary to the fuel marketer than distribution system additives. In general they will provide benefits which the motor industry or consumer should appreciate, and will often form the basis of advertising claims. It is because of the proprietary nature of much of this business that the additives are put into the fuel as close to the market as possible. This is especially important when many oil companies swap fuels to keep costs down.

Fuel additives and automotive fuels
(k.tons OECD Europe 1998)

	Gasoline	Diesel	Total
Fuel additives	83.8	80.1	163.9
Automotive fuels (estimated)	127,000	130,000	257,000

Fuel additive treatment rates are very small, and measured in mg/kg, whilst fuel consumption is measured in large volumes and is a major factor in modern society. Just as that society is changing, so are the needs and characteristics of the automotive fuels market.

3. Response to change

Although there may be some examples of change in the fuels and motor industries following directly from the development of a new chemical product, in general fuel additive development has taken place because of a recognised market need. The primary driving forces for change have been economic value to the consumer and (particularly over the last fifteen years) improvements to the environment.

Cost saving has always been a driving force for change within automotive fuels, and this has applied particularly to the distribution system additives which are discussed in more detail later. Sometimes cost saving and added performance are interwoven. Flow improvers for diesel fuels were originally introduced to give an acceptable pour point to otherwise unacceptable quality distillates, to enhance performance. But the market grew when it was realised that refiners could make more cost effective use of crude oil by cutting deeper into the barrel, and converting the low value residual fuel oil into high value heating oil or diesel fuel by the use of flow improvers.

Adding value to the consumer has over the long term been of rather more concern to the motor industry than the oil industry, although that has changed somewhat in recent years. Examples include improved performance (more power, better acceleration), reduced maintenance (improved engine cleanliness) and fewer mechanical problems which would cause the vehicle to be off the road (eg. fuel pump failure).

Response to environmental need has been particularly strong during the past fifteen years, much of the driving force being exhaust emissions legislation applied to the motor industry.

The importance of partnership has already been mentioned. This becomes even more vital as long-established values are being challenged. As the motor industry responds to pressures to reduce exhaust emissions, the use of fuel injection and catalysts become imperative for gasoline-engined passenger cars. Injectors require gasoline with detergent additives if they are to stay clean and give optimum fuel economy and emissions performance. Noble metal catalyst systems and oxygen sensors are sensitive to certain elements and this has to be allowed for. Alternative fuels have very different properties from conventional fuels and need special additive treatments.

A prime example of additive industry response to changing market conditions is provided by the introduction of environmentally friendly very low sulphur diesel fuels. These fuels have, because of the absence of natural lubricity, generated higher wear in fuel pumps leading to premature failure. The use of lubricity additives has restored the lubricity of these new fuels to that of more conventional diesel fuel.

Further changes generated by environmental need or other forces will undoubtedly follow. There will be an increasing need for industry and the legislators to make informed judgements balancing what may be major benefits against small disadvantages - perhaps a significant improvement in air quality to be balanced against the need for extra precautions in product handling.

3.1 The growth of road transportation

Although this paper does not attempt to cover the details of developments in the motor and automotive fuels industries, some brief mention must be made in order to put the development of additives in context. The use of hydrocarbon fuels in transportation is now an accepted part of most peoples' daily lives. More people travel, more goods are transported, more efficiently, more safely and with more consideration to the environment than at any time in the past. This has, however, not been easy to achieve and has been the result of the very significant efforts of:

The motor industry - developing the safe, fuel efficient and environmentally acceptable vehicles needed.
The oil industry - providing the quality and quantity of fuels required.
The additives industry -supplying the range of additives needed to enhance fuel quality during production, distribution and use.

The changing character of gasoline vehicles

The changing character of gasoline powered vehicles can easily be demonstrated by considering developments made with the standard family saloon (Figure 3).

Figure 3 The changing character of gasoline vehicles

Period	**1930s**	**1960s**	**1990s**	**2000s**
Capacity, litres	1.5 (side valve)	1.5 (ohv)	1.4 (ohc/16v)	1.5 (dohc/16v)
Compression ratio	5.5:1	9.1:1	9.5:1	9.4:1
Max. power, kW	22	30	70	75
Max. speed, km/h	96	136	184	185
Fuel Consumption, L/100 km	14	10	7	7
Octane requirement	70-75	97-100 (leaded)	95 (unleaded)	95 (unleaded)
Engine overhaul distance, km	8-25,000	50,000+	None	None
Catalyst	-	-	Yes	Yes
Emissions (idle CO, vol. %)	4-6	4-6	0.1	0.0025

Initially, many of the advances in power, performance and fuel economy were attributed to increases in compression ratio. In more recent years advances have been achieved by a range of engine and vehicle developments. The routine maintenance requirement of vehicles has declined. For example, the once routine annual decoke has, for many years, been a thing of the past. The introduction of catalytic converters has significantly reduced vehicle emissions. The use of electronics for engine management has allowed far more effective use of fuel injection equipment and improved fuel economy whilst helping to minimise exhaust emissions. The use of more than two valves per cylinder and accessories such as turbochargers has helped performance and emissions. The use of direct injection technology, initially in diesel passenger cars but now in gasoline-engined cars too, will improve fuel economy greatly, especially under low speed conditions.

The changing character of diesel vehicles

As one would expect, there have similarly been great changes in the performance of diesel vehicles, both passenger cars and heavy-duty trucks.

Figure 4. The changing character of diesel passenger cars.
(figures are approximate and for illustration only)

PERIOD	**1960s**	**1990s**	**2000s**
Capacity (litres)	2.5 OHV	1.9 OHC	1.9 OHC + 16V
Compression/Type	20:1 IDI NA	20:1 IDI NA/TC IC	20:1 DI/TC/IC/ (CR & UI)
Max power (kW)	40	70	100 +
Max speed (km/h)	120	170	200
Fuel consumption (L/100 km)	11	8	7
Engine overhaul (km)	160,000	None	None
Oil change period (km)	5000	15,000	30,000
Catalyst	No	No	Yes
Smoke/particulate level	Very high	Medium	Low

NA	Normally aspirated
IDI	Indirect injection
DI	Direct injection
TC	Turbo Charged
IC	Inter cooler
CR	Common Rail
UI	Unit injectors

Figure 5 The changing character of heavy-duty vehicles

Period	**1930s**	**1960s**	**1990s**	**2000s**
Gross weight, tonnes	5	15	44	40-60
Vehicle configuration	Rigid	Rigid	Articulated	Articulated
Engine type	6 cylinder NA/IDI	6 cylinder NA/DI	6 cylinder Turbo/DI	6/8 cylinder Turbo/IC/DI
Engine displacement, litres	6	6	14	11-14
Maximum power, kW	45	90	280	360
Specific fuel consumption, g/kW.h	420	320	200	180
Bosch smoke	4-6	3-4	1	<1

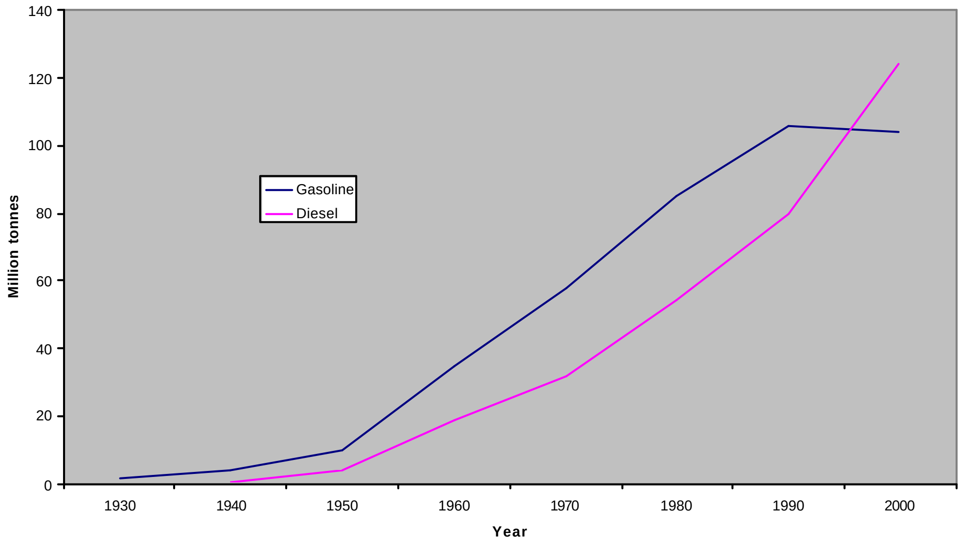
NA= Normally aspirated
Turbo = turbocharged
(I)DI = (in)direct injection

Payloads above 40 tonnes are now common throughout Europe. The use of large turbocharged engines, often with intercoolers, has provided the increased power needed, and has improved rated efficiency. Smoke and particulate emissions, although very significantly reduced, have not been eliminated and much recent and future legislation is focused on this point. In discussing the diesel engine, its growing importance as a power unit in passenger cars must not be overlooked. Modern diesel engines for passenger cars can provide outstanding performance. Their growing use in certain markets will, in part, contribute to the continued growth in diesel fuel use.

3.2 European oil industry trends

The demand for automotive fuels has continued to grow steeply (Figure 6)

Figure 6
European Gasoline and Diesel use (EEC12)



Gasoline consumption within the EU now exceeds 127 million tonnes a year and diesel fuel use at 130 million tonnes or so a year has now exceeded that of gasoline.

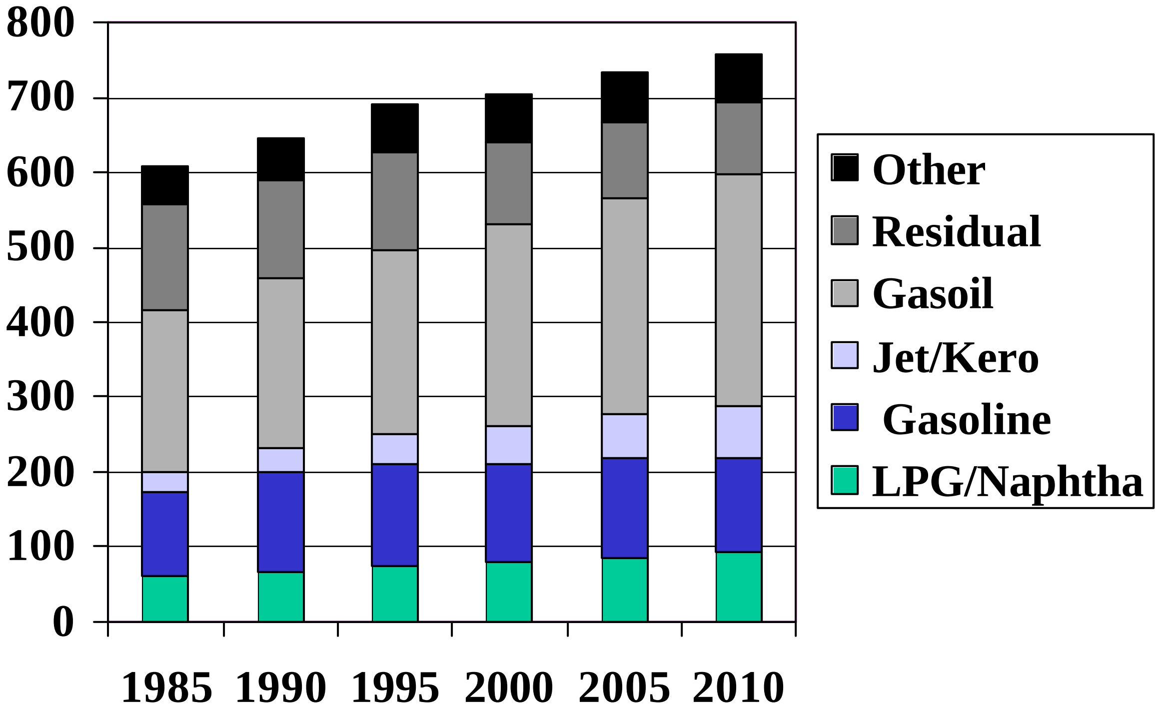
For many years the growth in use of gasoline and diesel fuel tracked the increase in crude oil consumption. Following the oil shocks of the 1970s, however, big changes in refinery operations were needed to produce more gasoline and diesel from less crude. Many small, simple refineries were closed. Those that survived were the so-called complex or conversion refineries which had the hardware to convert excess heavy fuel oil into light products.

These changes had a major impact on automotive fuel quality. The streams produced by conversion processes contain higher levels of olefins and aromatics than those produced by simple hydroskimming refineries. These hydrocarbons can cause problems of instability, engine fuel system fouling and poorer combustion characteristics. This change in fuel quality happened at a time when the market began to demand higher quality fuels.

The historical and predicted pattern of change is shown in Figure 7.

Figure 7 OECD Europe Oil Product Demand

Millions of tonnes



3.3 Development of fuel additives

What do fuel additives do?

Fuel additives perform a variety of functions and are now indispensable components of automotive fuels. Although this paper looks separately at gasoline and diesel fuels, the principles are the same for both. In general fuel additives are used to enhance the qualities of the base fuel or to add new required performances. Sometimes the incentive for use is to bring an unsatisfactory product up to an industry standard, whilst on other occasions use of an additive may allow satisfactory standards to be maintained at a lower cost, with raw materials being diverted to higher value applications such as chemicals or aviation fuel. On some occasions additives may provide benefits which are not present at all in the base fuel.

The benefits of additives may be valued by different parts of industry and society in different ways. Cost savings will be most relevant to the refiner and in the competitive market to the consumer. Added quality will be valued first by the motor industry, and secondly by the consumer. Environmental benefits will be appreciated by society as a whole.

European automotive fuel quality is defined by the European Standards EN228 (gasoline) and EN 590 (automotive diesel). These standards have traditionally not included most "performance" features provided by additives, but have included such important qualities as octane number (gasoline), cetane number and cold filter plugging point (diesel) which may be influenced by additives. In contrast, the relatively recent World Wide Fuels Charter(3) comprises specifications, produced by the worldwide automotive industry, which include several "performance" features which are measured in engine tests and require the use of fuel additives to give passing performance.

Major developments in gasoline additive use

The growth in gasoline additive use largely reflects developments in engine design and refinery operations.

Antiknocks were introduced in the late 1920s/early 1930s to provide the octane rating needed to enable vehicle designers to increase engine compression ratios to levels which gave acceptable efficiency and performance.

Antioxidants were introduced in the 1930s to combat the tendency of cracked blending components to oxidise and form gums. These products became significantly more important in the 1970s when increased use of catalytic cracking, to increase levels of gasoline and diesel production within refineries, also raised the levels of unstable olefinic compounds in these fuels.

More recently, detergent and dispersant additives have been increasingly used to reduce deposit build-up within the engine inlet system, and eliminate the potential performance and emissions problems such deposits can cause.

Major developments in diesel additive use

Again, diesel additive use reflects the impact of growing diesel fuel demand and the changing technology of diesel engines.

The introduction of wax crystal modifiers (flow improvers) was key to increasing diesel fuel availability. Without these additives, it is likely that in winter the performance of diesel vehicles could not be maintained without additional costs in refineries or vehicle fuel systems.

The changing pattern of refining in the late 1970s/early 1980s also had an impact on diesel fuel quality. The need to produce increased volumes of diesel fuel from reduced volumes of crude meant that low cetane cycle oils from catalytic crackers were blended into diesel fuel. Cetane improvers were then needed to maintain or increase cetane number, the key indicator of diesel fuel ignition quality, and their use became more common.

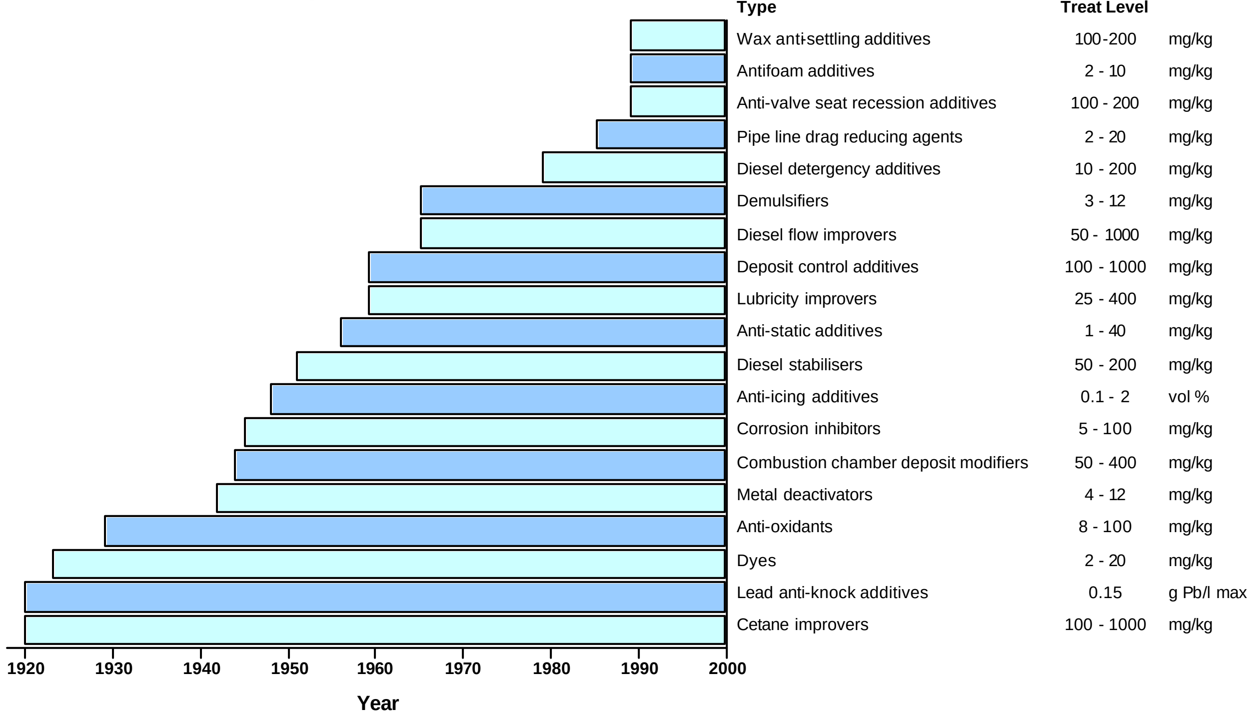
The move towards performance packages in the 1980s reflected the growing sophistication of the diesel fuel market and, particularly, the greater needs and expectations of the passenger car user. More recently environmental legislation has re-inforced the need for detergents to keep the engine clean and maintain emissions performance long-term. It has also, through the introduction of very low sulphur fuels, led to a need for lubricity additives.

Fuel additive types and history

An indication of the approximate dates of introduction of major fuel additive types is given in Figure 8.

Over the years a number of additives have been incorporated into automotive fuels to 'improve' their properties. The figure indicates the application areas for the different types of additives. It can be seen that new application areas are still emerging as new engines are developed by the OEMs, whether in response to technical improvements or to government legislation. In any particular fuel some but not necessarily all of the additives listed in the chart may be used.

Figure 8
Fuel additive types and history



NB. Treat levels vary and in this chart are indicative of active undiluted additive. When additive treatments are discussed the numbers quoted can be misleading. Some of the additives are high molecular weight species and have a high viscosity. This makes them difficult to handle with normal equipment. The additives are thus generally diluted with a hydrocarbon solvent such that the additive solution is easily miscible with the fuel. This can suggest treatment levels are high when in actual fact the active constituent levels are much lower.

4. Gasoline additives

In the following paragraphs, we give brief descriptions of the applications, treat levels and chemistries of the primary gasoline additives.

4.1 Anti-static additives(4)

Static electricity can build up during pumping operations both within refineries and at filling stations, and static discharges present an obvious fire hazard. This can be addressed by improving electrical conductivity and charge dissipation. In the late 1950s additives were introduced to facilitate this improvement.

The chemicals used are fuel-soluble chromium materials, polymeric sulphur and nitrogen compounds and quaternary ammonium materials. These improve fuel conductivity and reduce the potential for static build-up. Treat levels are very low, and typically only 2-20 mg/kg. Use is much more commonplace in fuels of intermediate volatility such as aviation kerosenes and low sulphur gasolines and diesel fuels are increasingly treated in certain markets now.

4.2 Metal deactivators (4)

Certain metals when solubilised in a nascent form by metal contact will form fuel-soluble salts. These salts promote oxidation in the fuel, with subsequent gum formation and deposit build-up in the fuel system. The function of metal deactivators, first introduced 60 years ago, is to prevent the formation of these salts.

The most widely used chemical is N, N'-disalicylidene -1, 2 - propanediamine, and its basic mechanism is to chelate dissolved copper. This chemical also migrates to any new/other surfaces, further inhibiting the formation of soluble metal salts. Again treat levels are very small, down to 4 mg/kg, as too are total volumes used mainly in aviation gasolines and kerosenes.

4.3 Dyes(4)

Dyes have been used for many years to distinguish between different commercial types of gasoline. They are used to distinguish products under different tax regimes, and to identify leaded/unleaded gasolines.

Coloration of gasolines is achieved by azo compounds and/or anthraquinone. The chemistry involved with petroleum dyes is similar to that of other dye applications and, in many instances, is outside the main activity of ATC member companies. Annual tonnages used in gasoline and diesel fuel today, at treat levels of 2-20 mg/kg, are estimated at 350 tonnes.

4.4 Demulsifiers (4)

Just as dyes are used for wider purposes than the identification of different gasolines, so too are demulsifiers. They do, however, have a specific purpose in distribution systems where finely divided water can create a haze and the formation of an emulsion. Such emulsions can have detrimental effects on gasoline quality and performance. Complex mixtures of nonionic surfactants are used within refineries as surface active materials which modify the surface tension. The coalescence of the water gives a clear liquid and avoids the formation of emulsions. Their use at treat levels of 3-12 mg/kg, is linked to deposit control additives, which tend to stabilise emulsions.

4.5 Corrosion inhibitors (4)

Water contained within gasoline, or infiltrating from external sources, combines with air to attack iron (and other metallic surfaces) to form rust. This can be inhibited by protecting metallic surfaces with an additive film, for which carboxylic acids, amines and/or amine salts of carboxylic acids are used. The polar portion of the molecule adheres to the metal surface, and forms the protective film required.

This technology has been available, and in use, for 60 years. More details of the chemistry are available in the previous ATC paper, Doc. 49(1). The current European market for corrosion inhibitors in gasoline/diesel fuel is estimated at 1250 tonnes per annum

4.6 Antioxidants (4,5,6)

Gasoline also contains unstable species such as olefins and dienes, and these can polymerise to form gums. The gums are carried forward into the engine system, and can lead to malfunctioning and breakdown. Such problems can be avoided by introducing antioxidant chemicals, at treat levels of 8-40 mg/kg, into products within the refinery.

Again the chemistry used has been available for many years, and is similar to that used in other applications such as lubricants.

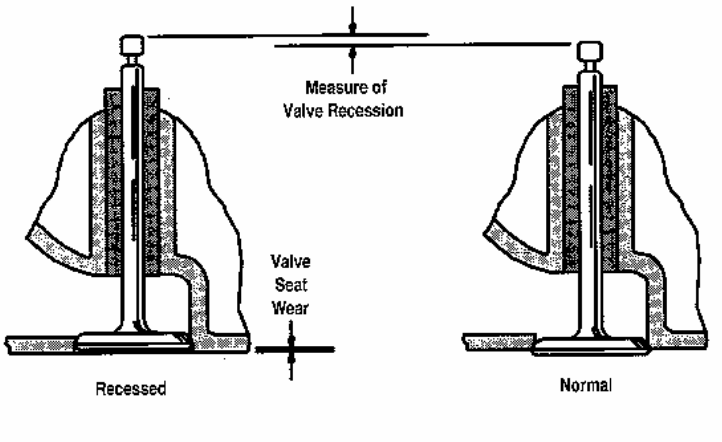
It comprises hindered phenols, aromatic diamines, or mixtures of aromatic diamines and alkyl phenols. Oxidation and polymerisation of olefins takes place through a free radical mechanism. Reaction with precursors interferes with gum formation in olefins, and achieves both fuel storage stability and cleanliness of engine fuel systems.

Antioxidants are the biggest single gasoline distribution system additive. Usage in Europe, however, is still low at 2200 tonnes per annum. They are also effective and used in aviation gasolines and kerosene.

4.7 Anti-valve seat recession additives

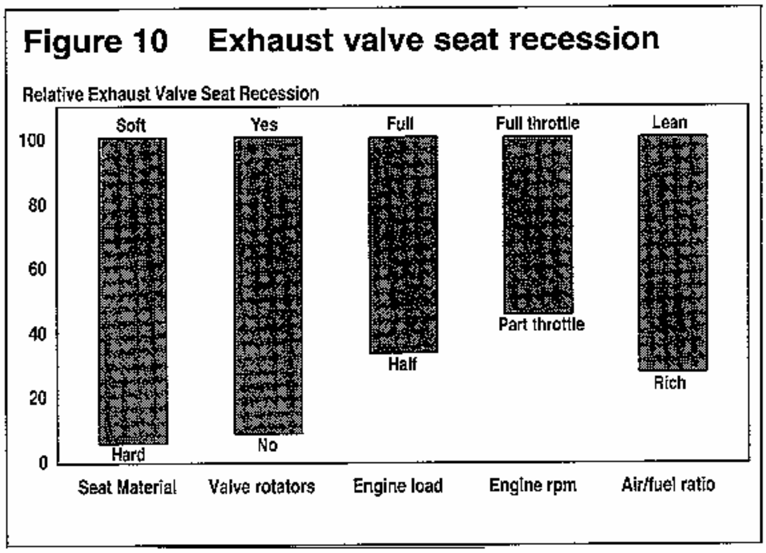
A well-known problem with unleaded gasoline is that, for certain old metallurgies, significant wear occurs in the exhaust valve seat. The lead additive, in addition to its primary purpose of increasing octane quality, also provides a critical wear-reducing function by depositing a thin protective layer of lead salts on valve seat surfaces. Without this protection, exhaust valve seats wear or recede into the cylinder head. This leads to poor valve sealing and loss of compression, and in turn results in loss of power, increased fuel consumption, rough engine operation, poor starting and increase in emissions, and ultimately severe engine damage.

Figure 9 **Exhaust valve seat recession measurement**



This effect is illustrated in Figure 9. Exhaust valve seat recession is measured by monitoring the increased height of the top of each exhaust valve stem above the top deck of the heads.

The extent of recession varies enormously among engine makes and duty cycle. It is a function of engine design and operating conditions. Recession is most severe at high load, high speed and lean operating conditions. Figure 10 illustrates the relative effects of some important hardware and operating parameters on valve seat recession.



The problem of valve seat recession can be overcome, by the use of additive chemistries based on potassium, phosphorus or manganese. The combusted metal salts act as a protective lubricant and prevent the direct metal-to-metal contact that would otherwise cause high wear. This protection is continuously maintained when the additive is added to the gasoline.

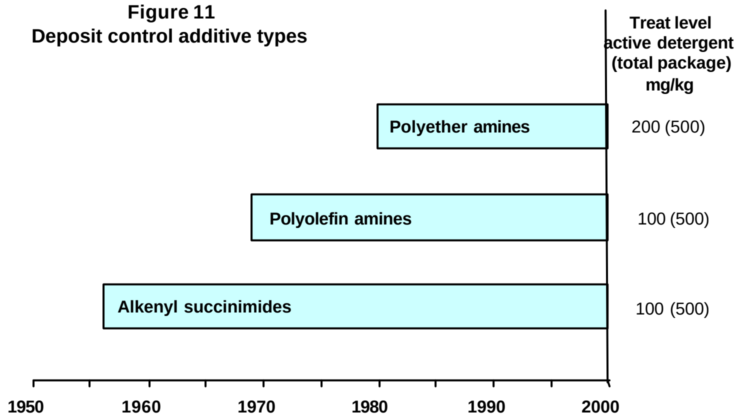
The use of these additives at treat levels of less than 50 mg/kg can keep older vehicles in service despite the elimination of leaded gasoline. With the phase-out of leaded fuel there was a growth in demand for these additives, but the market is declining again as these older vehicles are gradually scrapped.

4.8 Deposit control additives(7)

There is a full range of deposit control additives (DCA) designed to keep the whole fuel system completely clean and free of extraneous matter. They have been introduced over a period of time to address specific problems: but the general problem is that of deposits in the air/fuel inlet system which leads to uneven running, and poor fuel/air ratios which adversely affect power, driveability, fuel economy and emissions. The chemistries used include amides, amines, amine carboxylates, polybutene succinimides, polyether amines and polyolefin amines. Treat rates vary, with the detergent acting to disperse deposit precursors and carry them forward in a very thin liquid film into the combustion chamber. Many of these additives are used in conjunction with carrier fluids such as polyalphaolefins, polyethers, mineral oils and esters.

The first deposit control additives, used at very low levels, were long chain amides. They were introduced in the mid 1950s.

Figure 11
Deposit control additive types



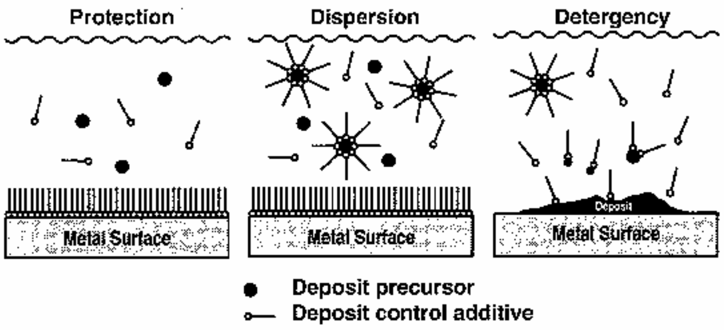
Alkenyl succinimides were then introduced as dispersants in crankcase lubricants towards the end of the 1950s, a short time after they were tried as detergent additives in gasoline.
These were the second generation of DCAs.

In the 1970's increased conversion of crude to transportation fuels resulted higher amounts of high olefin cracked stocks being used in gasoline blending. The quality of the gasoline, and in particular olefin content where higher levels can lead to a reduction in fuel stability, plays a big part in the treatment required for particular batches of fuel. This also corresponds to a time of increased susceptibility to performance problems due to fuel-derived deposits in engines tuned to meet tighter emissions requirements. Polyolefin amines were introduced during this time as being more effective deposit control agents. More recently, further developments have lead to the introduction of polyether amines (mainly in North America, Korea and Japan) and combinations of alkenyl succinimides or polyolefin amines with polyether based carrier fluids for improved cost-effectiveness.

Deposits are laid down in the pre-combustion areas of the fuel inlet system of all vehicles. The nature of the deposit can be sticky, soft or hard, and its position in the inlet system is a function of a large number of factors. These include the degree of oxidation/polymerisation, storage temperature, and contamination by blowby and exhaust gas recirculation. Deposits can also be derived from the crankcase lubricant. All of these deposits can affect the regulated and unregulated emissions of the vehicle(8), and its fuel economy. Other impacts are to startability, driveability, idling, and power.

Deposit control additives are generally long hydrocarbon chains attached to a polar head group. Deposit precursors are attracted to the deposit control molecule, and become bound into the dispersant miscelle. At normal operating temperatures the DCA is a liquid which forms a thin film throughout the inlet system. The thin film is driven forward by the air and fuel vapour flow, but forms a first line barrier to deposit precursors as well as a dispersant/neutraliser of the precursors protecting the metal surface. In the case of deposits on the metal surface, the liquid film slowly removes deposits with a detergent action.

Figure 12 Deposit control additive mechanism



The main areas where DCAs are effective are:

(a) Carburettors

Within the conventional carburettor system, deposits on the throttle body and throttle plate lead to restrictions in the air supply when the throttle is at or near the closed position. This then gives rise to rough idling and stalling, with a consequent impact on fuel consumption and increased exhaust emissions. Deposits in the jets affect all aspects of driveability in an adverse manner due to the disruption of fuel flow.

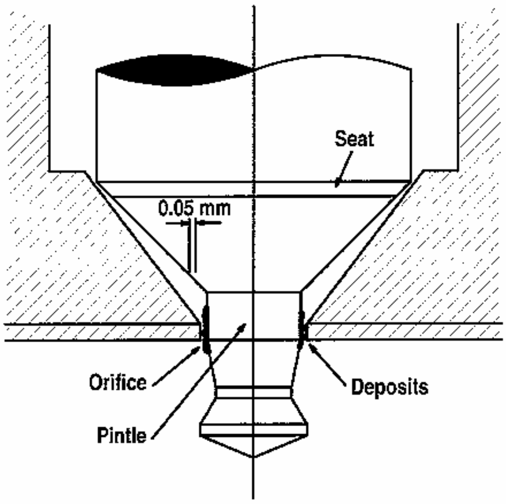
(b) PCV valves

The literature gives several excellent examples of how deposit control additives can clean up highly blocked positive crankcase ventilation valves to near their operating condition when new.

(c) Port fuel injectors (9)

Fuel injectors are very delicate metering devices, and monitor very precise amounts of gasoline. With such equipment it is important to maintain all of the surfaces over and through which the fuel/air vapours flow in a totally clean condition. If this is not achieved then, as with the carburettor, problems will occur.

Figure 13 Location of PFI deposits



- Appearance: a uniform varnish type layer with a black brittle nodular layer on top
- Thickness: 6 µm
- Mass: tens of micrograms
- Flow restriction: 26%

Figure 13 is a diagram of a typical port fuel injector nozzle, and the pintle tip is the operating area of most importance. The clearances to achieve the small quantities of fuel necessary for controlled additions are very small (0.05 mm), and any restrictions will result in serious operating difficulties due to disruption of the proper fuel/air ratio in the cylinder. Injector design is a critical factor in terms of susceptibility to the build up of deposits.

Gasoline is a mixed boiling range liquid, and when the engine is switched off fuel remaining in or near the pintle tips is subject to high heat soak temperatures. These high temperatures lead to the formation of free radical species, and then to a combination of auto-oxidation, chemical rearrangement and degradation of the remaining fuel. Sticky deposits ensue, trapping particles, and the degraded fuel contains longer molecules which act as deposit precursors. These precursors can be dispersed, as already explained, by detergent DCA.

There are two tests currently in widespread use by industry to evaluate a fuel and/or additive's injector cleanliness performance;

- ASTM D 5598 is a 2.2L turbocharged, four-cylinder DaimlerChrysler vehicle test. It is the test required by the U.S. EPA(8) and California ARB to certify additive performance for injector cleanliness.
- IFP-TAE-1-87 is a 1.6L, Peugeot 205 gti four-cylinder engine dynamometer test. This test is now essentially obsolete as the critical reference fuel is not currently available.
-

(d) Inlet valve deposits (10)

The fourth major area for deposit formation is the inlet valve, with resultant problems in power loss, decreased fuel economy, startability, driveability demerits, decreased power (increased acceleration times) and increased emissions.

Physical contributions to inlet valve deposits are numerous, and summarized in Figure 14.

Figure 14 Mechanism of inlet valve deposits - IVD sources

- **Atmospheric contaminants**
- **Engine blowby (PCV)**
- **Cylinder blowback**
- **Exhaust gas recirculation (EGR)**
- **Lubricating oil**
  - **Oxidised materials**
  - **Suspended insolubles**
- **Gasoline**
  - **Thermal and oxidation degradation materials**
  - **Gums**

Engine design plays a critical role both in terms of the tendency for deposits to build and the susceptibility of the engine management to be adversely affected by them. Within a particular engine design, the rate of build up of intake valve deposits on a given fuel is influenced mainly by valve temperature, which is a function of the operating cycle. The tendency of base fuel to form deposits has been loosely correlated with the aromatic and olefin content, the level of sulphur and the fraction of high boiling material in the blend. Other parameters such as the presence of oxygenates (e.g. ethanol) also play a role.

Intake valve deposits disrupt the proper air/fuel ratio by one of two ways. In the first, deposits accumulate to such a level that physical blockage of the intake manifold passage occurs, restricting air and fuel flow into the cylinder. These heavy deposits were common in carburetted engines and negatively impact power (acceleration time), fuel economy and emissions. In the second, which can occur with even relatively low levels of deposit accumulation, the deposit acts as a sponge, absorbing fuel into the pores of the deposit, then releasing the fuel through evaporation or desorbtion. This disrupts the flow of fuel at the proper timing interval into the cylinder and reduces droplet evaporation efficiency, thus creating an imbalance in the fuel/air mixture into the cylinder. These are the type of deposits typically formed in modern, port fuel injected engines, the primary negative effects of which include degradation of driveability, particularly upon cold start and warmup conditions, and emissions performance. Figure 15 presents a range of deposit levels on intake valves from port fuel injected engine.

Figure 15. Intake valve deposits.

Example showing the effect of detergent additives on inlet valve deposits

There are numerous intake valve deposit tests in use throughout the world. The four most widely used are summarized below:

Figure 16. Intake valve deposit tests

Test	Engine	Test Description	Typical Deposit (mg/valve)	
			Base Fuel	Additized Fuel
CEC F-05-A-93	MB M102E 2.3L	60 hr dyno	200-500	<30**
CEC F-20-A-98	MB M111 2.0L	60 hr dyno	150-400	<25
ASTM D 5500	BMW 318i 1.8L	16K km veh	290*	<100*, <50**
ASTM D 6201	Ford 2.3L 4-cyl	100 hr dyno	300-1000	<50**

* D5500 is the test required by the U.S. EPA(8) and California ARB to certify additive performance for intake valve cleanliness. These represent the minimum acceptable base fuel result and the maximum acceptable additized result for U.S. EPA. CARB require less than 50 mg/valve additized result.

** World Wide Fuel Charter recommendation, category 3/4.

(e) Combustion chamber deposits (11)

All spark-ignited (gasoline-powered) engines develop combustion chamber deposits (CCD) to some level. These deposits are the result of condensation of partially-thermally oxidized fuel, oil and additive components on the relatively cool piston and cylinder head surfaces, which then further react to form solid deposits. These deposits have been known for many years to negatively impact the octane requirement of an engine, which in a modern, knock sensor-equipped vehicle translates to a loss of power and acceleration. They have also been shown to be responsible for increases in NOx emissions while at the same time marginally improving fuel economy, due to the increased thermal efficiency brought about by the insulating properties of the deposits. In more recent years, the tighter tolerances and design changes incorporated in modern engines to accomplish ever greater demands for emissions, fuel economy and accleration performance has led to new phenomena such as “carbon rap” and CCD flaking-induced driveability problems.

These issues, and the inherent limitations on further improvement in engine design due to the need to allow for CCD, have led to pressure to minimize the contribution to CCD from all sources, including additives. To this point in time, in a bulk treat situation, the benchmark of additive performance is neutrality. That is, no increase in CCD is observed due to the additive beyond that from the base fuel alone. Some additives, in particular the polyetheramines, have shown the ability to reduce CCD below the level of base fuel, but only at very high doses typical of bottled aftermarket applications.

No generally accepted methods of effectively discriminating combustion chamber deposit performance exist. This is due to the much poorer "signal to noise" achieved in CCD measurements compared to, for instance, IVD tests. The difference between low and high levels of CCD may typically differ by only a factor of two or three, whereas acceptable and poor levels of IVD may differ by an order of magnitude. Procedures for measuring deposit thickness and mass have been added to standard IVD tests such as M102E and M111 and the ASTM D 5500 BMW and D 6201 Ford. Because of the lack of precision in these measurements and questions as to the applicability of the protocols for discriminating CCD, however, the benchmark of performance is typically not equivalence to base fuel, but an observed contribution of additive less than 40% above that of the base fuel. This is a standard that has been adopted by California ARB (using D 5500) and appears as a recommendation in the Worldwide Fuel Charter (Category 2-4, ASTM D 6201).

(f) Deposit control additives in direct injection spark ignited engines

The above observations on fuel related deposit formation in gasoline engines apply to conventional type carburetted and port fuel injected engines. In these engines gasoline and air are mixed well before entering the combustion chamber. In the late 1990s however, a new engine type was introduced, designated DISI (Direct Injection Spark Ignition) or GDI(Gasoline Direct Injection) as initially introduced by Mitsubishi. In these engines gasoline is introduced and mixed with air not before but in the combustion chamber, comparable to direct injection diesel systems. This has a significant impact on the fuel-related deposits in the pre-combustion areas and in the combustion chamber itself, compared to conventional type engines. A number of papers(12-16) have been published that have studied fuel and fuel additive effects in these engines and the impact of engine operating conditions.

In the absence of fuel, and therefore the fuel-borne additives – conventional DCAs cannot be effective in the pre-combustion areas, i.e. the intake valves and manifold. Although fuel is absent, the inlet system and valves have been shown to develop oil, EGR, PCV and blowback-derived deposits. The impact of these deposits is restricted to those given in the IVD section above for "heavy" deposits, that is to say a physical restriction of air flow into the cylinder.

With respect to the fuel injectors, studies have shown both the occurrence of injector deposits and a negative impact on engine performance. The effect is at least as critical as in PFI engines because the fuel spray quality directly affects the combustion quality. These same studies have shown that conventional DCAs have the capability to keep clean and clean up DISI injector deposits.

The effect of combustion chamber deposits in DISI engines is also critical to combustion quality, as excessive deposits, particularly in the piston bowl area, can lead to disruption of fuel evaporation and air flow patterns. In contrast to PFI vehicles, however, it has been shown that conventional additives can reduce deposits in this critical piston bowl area of the combustion chamber. The effects of DCAs in the other areas of the combustion chamber appear to be very similar to the effects in conventional type engines.

5. Diesel Fuel Additives

5.1 Wax crystal modifiers/middle distillate flow improvers (17) and Wax Anti-Settling Additives

(a) Background

This is the largest volume market for diesel fuel additives and the most mature. Products were introduced first into the Canadian market as pour point depressants but showed rapid growth in Europe from the late 1960s as diesel fuel flow improvers. The products are now sold worldwide but the European market is by far the largest. It is a seasonal market with products being used almost universally in the winter, and widely in the summer.

(b) Purpose

Middle distillate flow improvers (MDFIs), the most commercially important of the wax crystal modifiers, are the principal distillate additives used in refineries. Their use is driven by refining economics. In simple terms, MDFIs allow heavy fractions in the crude to be used in diesel fuel without adversely affecting the fuel's cold flow properties.

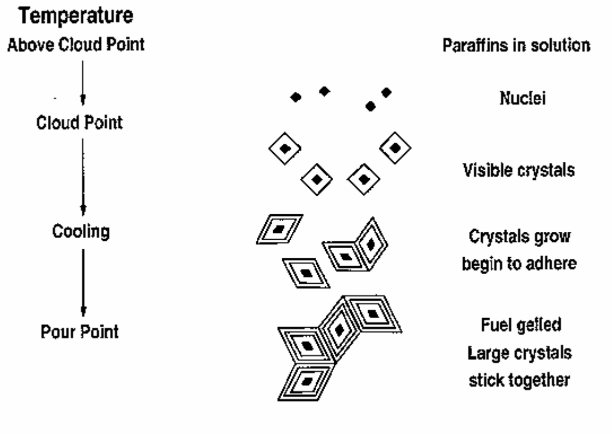
This means that more diesel fuel and less residual fuel oil can be produced from a given barrel of crude. This makes efficient use of a limited natural resource and helps keep down the cost of fuel production. The value of MDFIs, in terms of improved refinery economics, is large relative to the cost of the additives themselves. In 1992 it is estimated that for Western Europe the saving in refinery costs resulting from MDFI use amounted to US$1.5 billion (including both diesel and heating oils).

(c) Mode of operation

All crude oils contain normal paraffins in varying amounts. When crude is distilled, paraffins are contained in the distilled products, with diesel fuel/heating oil fractions typically containing 20-40% n-paraffins. The distribution of n-paraffin carbon numbers is usually in the range C_{10}-C_{30}.

In some respects these paraffins are very desirable in diesel fuel as they have a high cetane number and burn with low emissions. However, paraffins are the least soluble components in diesel fuel. When a diesel fuel is cooled, wax crystals form in the fuel. If the fuel is cooled further the fuel solidifies and the wax crystals crosslink to form a rigid matrix (Figure 18).

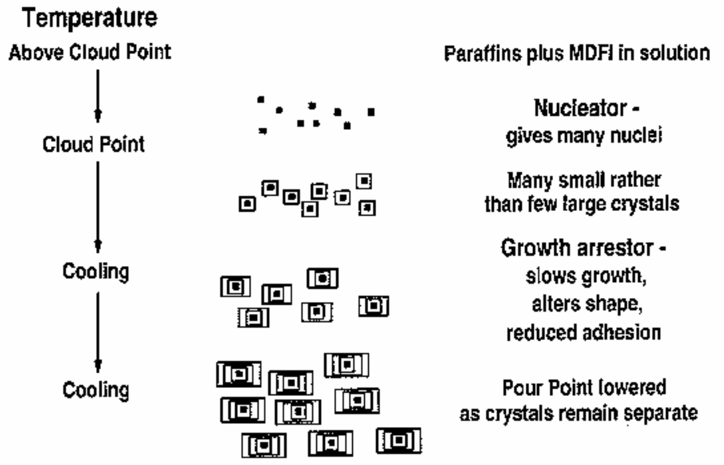
Figure 18 Wax crystal growth Without additive



Uncontrolled, wax crystallisation in diesel fuel can cause vehicle operability problems. Blockage of filters and narrow lines leads to fuel starvation with a loss of power and ultimately vehicle failure. The lift pump is typically protected by a 100 mesh filter and the injection pump by a 5-10 µm filter. It is possible for refiners to formulate diesel fuels meeting cold flow requirements without additives. However, this would be achieved by downgrading part of the diesel fuel into lower value products such as heavy fuel oil. This approach would be both costly and wasteful of a valuable resource.

Middle distillate flow improvers modify wax crystal size and shape so that they pass more easily through filters and lines in vehicles (Figure 19). They are typically added to fuel at 50- 1000 mg/kg.

Figure 19 Wax crystal growth
With additive



When the fuel cools down, the polymer molecules co-crystallise with the n-paraffins, blocking off crystal growth faces and forcing new crystal nuclei to form. They also act to modify the crystal shape. The net effect of the use of MDFIs is that relatively few, large flat crystals are converted into a large number of very small crystals.

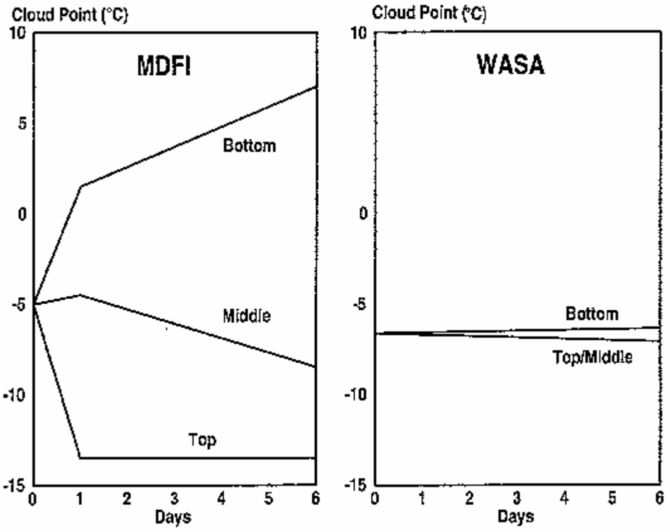
As well as causing problems in vehicle systems, these same wax crystals, which have a slightly higher density than the rest of the fuel, can cause problems in storage tanks. If the fuel is stored at temperatures below its cloud point for an extended period, wax will tend to settle at the bottom of the storage container. When this occurs, there is a risk that highly wax-enriched fuel will be delivered to some customers.

Wax anti-settling additives have been used selectively at a typical treat rate of 100-200 mg/kg since the late 1980s to obtain improved cold flow performance over and above that achievable with conventional MDFIs. The performance benefit is to:

- provide customers with premium fuel quality; or
- enable safe relaxation of cloud point to higher levels whilst still maintaining the required market performance.

Wax anti-settling additives (WASA) reduce the wax crystals to even smaller size than conventional flow improvers. The way in which WASA prevents wax settling in diesel fuel stored at a temperature below its cloud point is illustrated in Figure 20.

Figure 20 WASA reduces tendency for wax settling



(d) Chemistry

Middle distillate flow improvers are ashless low molecular weight co-polymers. Ethylene vinyl acetate co-polymers were the first products to be used and are still the mainstay of the industry, although other products are now also used including polymers in biodiesel.

(e) Test methods

Several tests are used in defining the cold flow properties of a fuel. The cloud point is the point at which the first wax crystals become visible. The pour point is defined as being 3°C above the solidification point of the fuel, and describes the lowest temperature at which the fuel is fluid.

Both tests are rapid, but the cloud point is generally too severe as an operability test for additive treated fuels and the pour point gives results which are too optimistic for diesel fuels.

The cold filter plugging point (CFPP) (EN 116/IP 309) is currently the most important cold flow test. It is defined as the lowest temperature at which a fuel is filterable under standard conditions. The CFPP was developed from field trial data and designed to reflect the lowest temperature at which the majority of vehicles would operate. The CFPP is considered a valid test where the difference between cloud point and CFPP is 10°C or less.

5.2 Corrosion inhibitors

All fuel systems are prone to corrosion with time, particularly when entrained or dissolved water is present. If corrosion is left unchecked, the corrosion products such as rust will block fuel filters, and pipelines and other parts of the distribution system will have reduced life.

Typical products are carboxylic acids, amines and amine salts of carboxylic acids. The additive is generally used at a treat level of 450 mg/kg for a commercial product. The polar portions of the molecules adhere to the metal surface and the whole additive forms a protective film.

5.3 Demulsifiers (18)

These are generally used in combination with diesel fuel detergents. Detergents on their own are powerful surfactants, and in wet distribution systems they can cause the formation of undesirable fuel-water emulsions and hazes. Demulsifiers effectively counter these side-effects.

Typical chemistries include alkoxylated polyglycols and aryl sulfonates. These are typically used at treat rates in the range of 10-20% of that of the detergent.

5.4 Antifoams (18)

All diesel fuels have a natural tendency to produce foam when pumped from a service tank into a vehicle's tank. For trucks this is not a problem, but it can be for passenger cars, with small tanks and narrow filter pipes, when overflow during fuelling can occur.

This irritating aspect of fuel performance can be improved by the addition of a small amount of antifoam to the fuel. These polysilicone-based compounds are effective at very low treat rates. Antifoams are usually added as part of a multi-functional package.

5.5 Diesel fuel stabilizers (19)

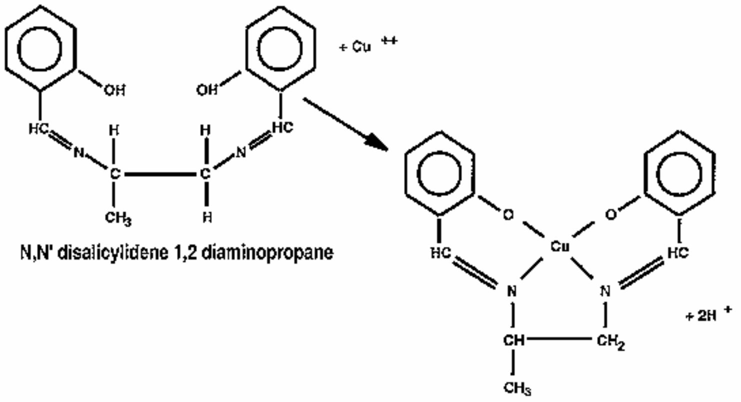
Diesel stabilizers were originally developed as refinery additives as an alternative to hydrotreating. The progressive lowering of diesel sulfur levels has largely eliminated stabilizers in this role. In recent years, however, they have increasingly been used as components of multifunctional packages.

Diesel fuel can be stored for prolonged periods. This is particularly so for military use where it is of prime importance that the fuel remains fit for use throughout the storage period. If the fuel contains trace amounts of olefins, nitrogen compounds, organic acids, or dissolved metals, the fuel may degrade. Fuel can become dark, and in extreme circumstances throw gummy deposits out of solution which may block filters. The problem can be mitigated by diesel stabilizer additives, which are typically used at treat levels of 50-200 mg/kg.

Several chemistries may contribute to fuel stabilisation and different components perform specific functions. Antioxidants act to inhibit the reactions that form sediment. Dispersants act to suspend any sediment particles that do form and prevent them from agglomerating and becoming a problem. Lastly, metal deactivators inhibit any trace amounts of dissolved metal, particularly copper, which otherwise could catalyse the instability reactions.

Stabilizers are generally long chain and cyclic amines. Antioxidants are typically hindered phenols or phenylenediamines. Dispersants could be ashless succinimides or polymeric methacrylates. Metal deactivators include N,N'-disalicylidene- 1,2 propanediamine. Figure 21 shows the basic chelating reaction between metal deactivators and dissolved copper ions. The copper ions are caged, reducing their ability to catalyse instability reactions.

Figure 21 The chemistry of metal deactivators



Details of some diesel fuel stability test methods are shown in Figure 22.

Figure 22 Comparison of diesel stability test methods

Test method	Conditions	Max allowable sediment limit	Correlation with field
Field storage	Ambient for 1 year	2.0 mg/100 ml	100%
ASTM D 4620	3 months at 43°C in dark storage, fuel filtered & sediment found	2.0 mg/100 ml	90%
ASTM D 2274	Oxygen bubbled through fuel at 95°C for 16 hours, filtered & sediment found	1.5 mg/100 ml	Not established
ASTM D 6468 **(Thermal pad)**	Heat to 150°C Test for 90 minutes, fuel filtered and rated 1-20 (also a % reflectance measurement)	max 7 rating	Not established

5. 6 Colour stabilizers

In most cases, diesel fuel is required to meet a specification for sediment stability. Some markets, however, such as Japan and Taiwan, demand water-white diesel fuel and colour stability is of prime importance.

The mechanisms of colour stability are even more complex than those of sediment stability. Tiny amounts of optically active compounds can influence the colour of a fuel. Whilst diesel stabilizers can be effective in controlling colour, their performance tends to be unreliable and where maintenance of colour is required, alternative means, such as clay-filtering, are needed.

5.7 Detergents[20]

(a) Background

All diesel engines use some form of fuel injection. Most small diesel engines used to use a system called indirect injection (ID1) while larger engines used and still use direct injection (DI). Today, most modern passenger car diesels have switched to DI. IDI tends to be smoother and quieter, while DI is more fuel efficient. The fuel injector sprays the diesel fuel into hot, compressed air, and the mixture auto-ignites. Efficient metering, atomisation and fuel-air mixing are key requirements for good combustion and especially important for low levels of exhaust emissions.

Modern diesel injectors are designed to exacting standards and form an integral part of the process for optimising fuel combustion. Their flow characteristics are set to allow a small pilot injection of fuel to initiate combustion, and then inject progressively more fuel into the burning mixture. Low needle lift gives pilot injection to initiate combustion. The main portion of the fuel is not injected until the end of needle lift. Such an approach provides a low rate of pressure rise and smoother combustion.

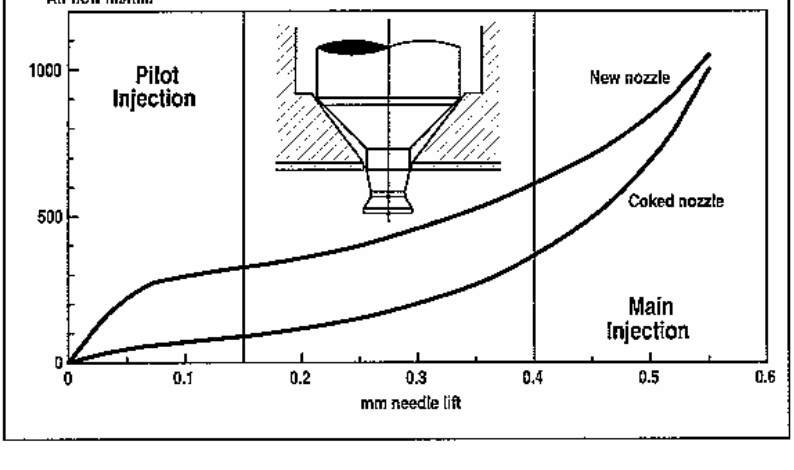
Clean fuel injectors are critical for efficient engine operation. A well dispersed spray pattern maximises fuel-air mixing, while good atomisation ensures rapid, efficient combustion.

All diesel fuels, but especially those containing products from conversion processes, have a tendency to lay down a small amount of coke in the annulus of the injector. This coke is thought to be caused by the thermal decomposition of unstable compounds in the fuel. It is such a common problem that injectors are designed to tolerate a certain level of coke. However, many of today's diesel fuels give excessive levels of injector coking, disrupting the fuel spray pattern and degrading atomisation. Higher emissions, noisier engines and a decrease in fuel economy are the result.

The importance of diesel detergents has been recognised by a statement in EN 590 which 'recommends suitable fuel additives without harmful side effects........ to help to avoid deterioration of driveability and emissions control durability'. The specification then says 'Deposit forming tendency test methods suitable for routine control purposes have not yet been identified and developed.' In other words, the only reason that detergent use is not mandated in the specification is the lack of suitable tests to measure and enforce it. However, with this text present, all responsible diesel fuel suppliers are including detergent additives in their products.

Figure 23 shows the design of a typical pintle nozzle and its flow characteristics.

Figure 23 Pintle type fuel injection nozzle and typical flow rates



(b) Purpose

The problem of excessive injector fouling can be controlled by the addition of detergents to the diesel fuel. Over the last decade these have been increasingly used by oil companies to keep injectors clean, and so maintain exhaust emissions and fuel economy at optimum levels. Fuel detergents help to prevent the formation of deposits on the injector nozzle partly by providing a film on the metal surface and partly by forming a protective coating around the developing deposit precursors.

(c) Chemistry

Diesel fuel detergents are predominantly succinimide and other ashless polymeric products having some family similarity to the dispersants used in gasoline and automotive lubricants. Details are proprietary to individual manufacturers. Typical treatment levels (usually in combination with other components in multi-functional packages) are 10-200 mg/kg.

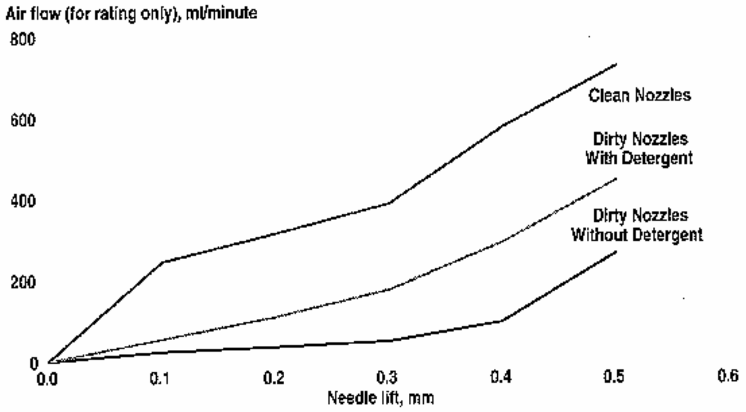
(d) Test methods

As injector coking only happens in the high temperature environment of the cylinder, the most widely used method to assess the performance of a detergent is by the use of an engine test.

The critical features of most of the industry tests are to measure the flow characteristics of clean nozzles, run the engine for several hours and then measure the flow characteristics of the dirty nozzles. The average level of coke-induced flow loss is then calculated.
Several procedures can be used to assess detergents, but the current European benchmark test is the Peugeot XUD-9A/L procedure. This is a ten hour test (CEC F-23-A-00) and is considered a severe test of a detergent's ability to prevent injector fouling. Evidence of performance in this test is a requirement of the World Wide Fuel Charter(3).

Figure 24 shows the performance of a detergent in controlling injector fouling.

Figure 24 Diesel detergents and injector coking - Peugeot XUD-9A/L test



5.8 Cetane improvers

(a) Background

As discussed earlier, the diesel engine is a compression -ignition engine and relies on the diesel fuel to auto-ignite to begin combustion. Ignition delay is the time between injection of the fuel into the cylinder and the onset of combustion. If the delay is too long, combustion is more violent (and hence noisier) and less efficient (causing high levels of exhaust emissions and poor fuel economy).

The ignition delay characteristics of a fuel are measured on a single cylinder CFR engine (ASTM D 613) which measures the compression ratio for a fixed ignition delay. In Europe cetane quality has traditionally been good, and refineries generally find it more convenient to predict cetane quality rather than measure it on the CFR engine. Cetane number correlates reasonably well with a fuel's density and distillation characteristics. Predicted cetane number, as opposed to measured cetane number, is referred to as cetane index. It has the advantage that it is very convenient, but it only predicts natural cetane number and does not indicate the benefit of cetane improver additives in the fuel.

(b) Purpose

Whilst cetane number is defined in terms of the ease with which a fuel ignites, cetane quality impacts directly on many aspects of engine performance. Engines operating on fuels with a low cetane number are difficult to start, especially in cold weather, noisy, emit high levels of white smoke and hydrocarbon pollutants at start up, produce less power and consume more fuel. High cetane numbers are therefore desirable. This has been recognised by the European legislators who have raised the minimum cetane number of EN 590 fuel to 51.

Aromatics conversion to naphthenes and paraffins through high pressure hydrotreating is a way to achieve higher natural cetane. However this process is very expensive and few European refineries have the necessary hardware to do this today. Cetane improver additives offer a more cost effective way to achieve higher cetane numbers. They can also help to improve refinery profitability by allowing more naphthenic crudes to be processed, and a higher percentage of low-value cracked components to be used in diesel blends.

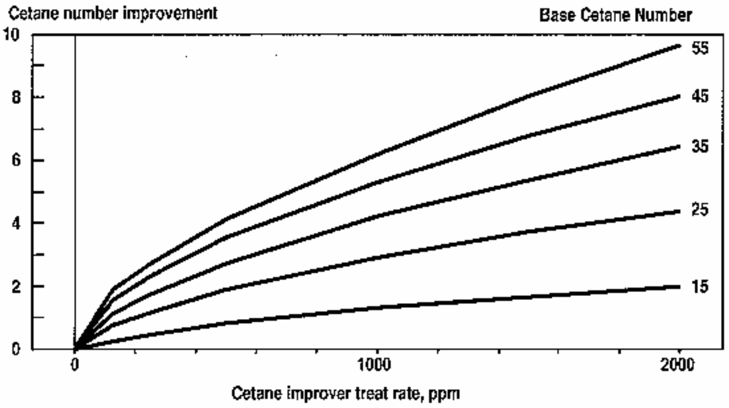
(c) Method of operation

Cetane improvers are alkyl nitrates of which 2 ethyl hexyl nitrate is most commonly used. They breakdown during combustion to form free radicals, which increase the rate of decomposition of the fuel and so reduce ignition delay. Such additives have been used for seventy years, most recently as components of multifunctional packages.

(d) Test methods

Cetane number (ASTM D 613) has already been mentioned and typical response curves are shown in Figure 25.

Figure 25 Cetane improver Typical response



Cetane number is, however, not an end in itself but a means to an end, and increasingly oil companies value the effects of cetane improvers on cold starting and emissions.

Figure 26 Effect of cetane number on cold start at -10°C

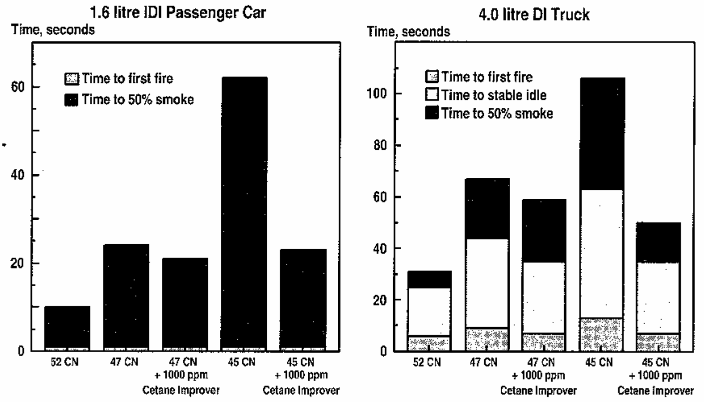
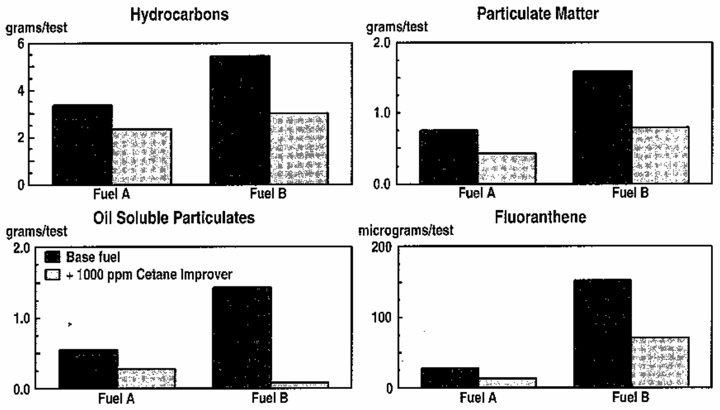


Figure 26 shows how cetane improvers enhance the cold startability of both diesel passenger cars and trucks. In addition to reducing the time spent by the starter motor cranking the engine, the cetane improver also reduces the time spent producing the unburned hydrocarbon seen in exhaust as white smoke.

Even under normal climatic conditions the presence of cetane improver in a fuel can reduce emissions. Figure 27 summarises a series of tests carried out using a typical IDI engine. Hydrocarbons and total particulates are reduced, as are the most harmful parts of the particulate matter.

Figure 27 Impact of cetane improvers on emissions



5.9 Lubricity improvers

Diesel fuel injector pumps often rely on the fuel itself to lubricate their moving parts. Until recently and under most circumstances, the properties of the fuel are such that this has not been a problem.

However the advent of low sulphur diesel fuels (roughly below 500mg/kg) in order to reduce exhaust emissions has changed the picture completely. Sulphur, aromatics and other polar compounds in the fuel act as natural lubricants. These helpful products are removed by the severe refining processes (primarily hydrotreating) used to produce the fuel qualities now required by national and EU specifications. The problems are made worse, the more the sulphur is extracted - and latest draft specifications are calling for 10 mg/kg or less.

The need to determine a new property of diesel fuel (lubricity) has required the development of a new test method. The High Frequency Reciprocating Rig (HFRR) is the test method of choice for Europe and most of the world. In the test, a ball under load is vibrated against a metal flat immersed in the fuel. The depth of wear of the flat is measured. The European diesel fuel Standard EN 590 now includes an HFRR wear scar limit of 460µm maximum which has been shown from extensive field tests to give an adequate degree of protection to fuel pumps.

The problems of poor lubricity can be solved by the use of lubricity additives. These long chain polar compounds give a mono-molecular coating on metal surfaces and protect against scuffing wear. Although the use of these additives in diesel fuel is relatively new, they have been used for over thirty years in jet fuel which also gives pump lubricity problems.

They have also been used for over thirty years in specific types of low viscosity diesel fuel in Sweden, similar in quality to the city diesel fuels of today.

The additives are surface active and form a boundary layer or cushion on the moving metal parts. Several proprietary ashless longchain polar compounds are currently in use. Typical treatment levels are in the range 25-1000 mg/kg.

5.10 Multifunctional diesel additive packages (21)

The previous sections have described in detail the various types of distribution and vehicle fuel system additives. It has also been mentioned that many of these additives are applied commercially in the form of multifunctional or Premium Diesel additives.

There are several reasons why oil companies improve quality with additives rather than by improving refinery processing. Refinery processing tends to be expensive and new plant often requires several years to bring on stream. Also, as distribution from refining centres requires inter-company product exchanges, improved fuel from one company would effectively be given to all other companies it exchanges with. This does not allow product differentiation.

Additives, on the other hand, are relatively cost-effective and can be put into the market very quickly. The flexibility provided by additives allows oil companies to brand fuel by emphasising different aspects of quality. What is more, additives can improve certain qualities which just cannot be adjusted by refinery processing, e.g. fuel foaming. They can also address specific concerns from motor manufacturers.

Package composition

Multifunctional additive packages may contain any or all of the following: detergents, cetane improvers, fuel stabilizers, flow improvers, antifoam, reodorants, demulsifiers, corrosion inhibitors, lubricity additives, and solvents for package stability. Typical treat rates are in the range 100- 1500 mg/kg.

5.11 Fuel-borne catalysts for diesel particulate filter regeneration

Current and future legislation on emissions of particulate matter from light duty diesel vehicles has resulted in certain OEM’s using particulate filters to control particulate emissions from certain vehicle models.

Routine in-service regeneration of these filters is essential to prevent excessive soot build up on the filter and the associated problems of back pressure build-up on vehicle operation or uncontrolled filter regenerations, with high temperature exotherms, on filter durability. Fuel-borne catalysts, typically certain cerium and iron compounds, are an effective additive route to achieving this.

6. Risks and benefits: The environmental balance

This section deals with the risks and benefits ensuing from the use of fuel additives, and tries to illustrate an environmental balance between these two aspects. Risks to man are addressed, but the main focus of ATC studies has been the environment.

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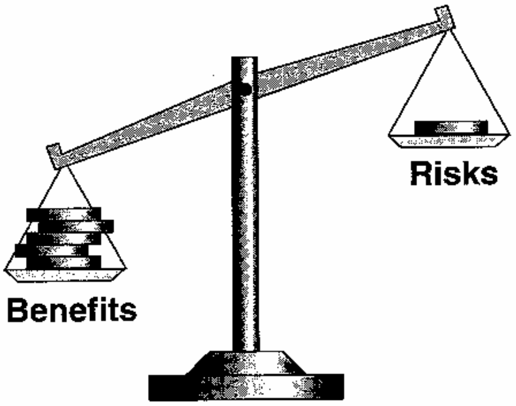
Clearly there are hazards involved in the handling and use of chemicals, and these are widely known and well documented. ATC document 43(22), revised September 2000, gives a listing of all possible classifications of the main categories of additive components. All of these components can be considered as of relatively low hazard to both man and the environment. Volumes also are low relative to the chemical industry as a whole, and the risks involved in the handling and use of fuel additives can therefore be assessed as small. There are nonetheless concerns with some petroleum additives and the solvents which may comprise a portion of typical fuel additive preparations, principally dermal irritation and sensitization (for man) and ecotoxicity (for the environment). These, together with emissions to the main environmental compartments, are discussed and quantified below.

At the same time there is an analysis of the benefits derived from the use of fuel additives. The need for additised fuels in the modern engine, and the added value these offer, have been touched upon above. Section 6.3 attempts to summarise and quantify them in terms of energy conservation, air quality improvements, cost savings and overall advantage to the public. It is ATC's belief that the environmental benefits, especially with regard to improvements in fuel combustion efficiency and reduced exhaust emissions, clearly and significantly outweigh any of the risks attendant on the use of fuel additives.

Figure 28 **Environmental balance**



6.1 Hazards

6.1.1 Hazard assessment

Under the Seventh Amendment (92/32/EEC) of the Dangerous Substances Directive, more than half of the main classes of petroleum additive components are not classified as dangerous: another 20% are classified as no more than irritant (21). Of those more severely classified, the major hazard is that of skin sensitization. There is, however, no anecdotal evidence of problems ensuing from the use of fuel additives in the workplace, and concentrations of any sensitizing substances within additive packages are usually sufficiently low (<1%). Those chemicals in pure form which are classified as skin sensitizers have proven not to invoke a skin sensitization reaction in animal tests so as not to require classification or labelling of their commercial preparations as potential sensitizers (23).

The “Dangerous for the Environment" classification and labelling scheme has only just been introduced for preparations (1999/45/EEC), and methodology for assessing the ecotoxicology of preparations has not yet been finally agreed. In anticipation of this requirement, however, and in line with ATC member company commitment to proper testing and full disclosure of relevant data to customers and consumers, a major ecotoxicology programme has been undertaken in conjunction with the ACC (American Chemistry Council) in the USA. Final results are not yet available. Preliminary findings, however, indicate a range of ecotoxicity. Test results on fish, daphnia, and algae, and activated sludge respiration inhibition data, are routinely used to classify the active ingredients of fuel additives individually and thus help to quantify any potential environmental effects that might be associated with fuel additive preparations. It is noteworthy that solvents common to most fuel additive preparations are typically toxic or harmful to aquatic organisms and should be managed with the same care given to refined gasoline fractions in this regard.

Assessing the hazards of the by-products from additive usage is less easy. Much is known of transformation products (see previous paper(1) Table 13), but there are some gaps in knowledge as products move further down the use chain and out of ATC member company control and responsibility. Concerns obviously relate to tail-pipe emissions, and the small contribution made to these from fuel additives is assessed in the fate analysis below. It is important to keep in mind that fuel additives ingredients typically comprise no more than 50 – 400 mg/kg of a typical combustion fuel. These ingredients are almost entirely consumed during the combustion process and mainly form CO_2 and water in the combustion process. CO and NO_x are also expected, but fuel additive contributions to any unburnt hydrocarbon emissions are negligible. Elsewhere research continues on unregulated emissions and the risk they present to man and the environment, but there is no evidence linking the very low levels of emissions due to fuel additives to the combustion process as a whole.

6.1.2. Hazard management

Even the relatively low hazards presented by fuel additives can be further minimised by proper management and regulatory compliance. ATC member companies are committed to that as a minimum, and continue to be fully prepared to disclose all relevant data under appropriate terms. Those terms include respect for commercial confidentiality when disclosing to regulatory authorities, or supplier/customer privilege in respect of specific products.

Since 1981 all new substances placed upon the EU Market at or above 1 MT per annum have been notified with a base-set of data in accordance with the Dangerous Substances Directive (67/548/EEC) and subsequent amendments. Both components and packages (under the Dangerous Preparations Directive (1999/45/EEC) are classified and labelled accordingly. Users are further protected by the issuance of safety data sheets (SDSs) as per 2001/58/EEC, which not only identify hazards and physico-chemical properties but also give handling advice, emergency measures, waste management direction, toxicological information, and specific recommendations for safeguarding the environment. ATC Member Companies are committed to having available all appropriate testing data, and each company issues their own SDSs for all products placed upon the EU Market whether classified or not.

Further control is exercised through adherence to workplace regulations which safeguard employees and minimize any potential for environmental contamination and harm. Potential future sources of emissions to the environment are being addressed by new regulations. These and other related aspects associated with any potential for long term environmental impact of fuel additives are being addressed by ATC/ACC ecotoxicology testing described above and future testing programs now under consideration. In these several ways risks to both man and the environment are effectively minimised.

6.2 Fate analysis

With fuel additives the product use cycle is not complex. Exposure to man and the environment can occur through leakage/spillage, both in the supply, transportation, chain and during use. These are, however, small and not dealt with in this paper.

It is worth reiterating here that fuel additive treat rates are measured in mg/kg and additive consumption is very small relative to the consumption of fuels themselves. It is also worth reminding the reader that by far the greatest proportion of any fuel additive consists of carbon, hydrogen and oxygen, with some other elements such as nitrogen.

For the initial issue of Document 52, ATC developed a model predicting combustion products of additives and representing them as a proportion of the total emissions from gasoline and diesel fuel use. The data obtained and reported clearly showed:

a) Fuel additives make no overall deterioration in emission levels
b) Fuel additives contribute less to tail pipe emissions than lubricant additives
c) Fuel additive carbon content is not significant when compared to fuel carbon and CO_2 and CO emissions from the fuel itself
d) Emissions resulting from the use of fuel additives are very small relative to the major reductions achieved over the last 20 years in regulated emission levels
e) Fuel additives do not appear to contribute to unregulated emissions

Since the initial issue of Document 52 much more detailed studies on this topic have been undertaken and reported. Possibly the most authoritative is that commissioned by the German Umweltbundesampt (Environmental Protection Agency) to assemble and evaluate known data concerning relevant mineral oil additives and their products and completed by the Fraunhofer Institute(24).

This study confirms all of the findings of the earlier ATC work and in particular concludes:
‘In the area of fuel additives there is a net positive influence reducing exhaust gas emission results. This is primarily not connected to distribution system additives but with the quantitatively significant detergent/dispersant substances. These prevent the formation of deposits in critical areas of carburettors, valves and injection jets. By appropriately structured test programmes, advantages in the area of the CO, HC, NO_x **and particulates formation can be proven. Fuel savings between 2 and 3% appear realistic**.’
In view of this and other independent work no update on the initial ATC predictions is considered necessary.

6.3 Benefits

Introduction

It is difficult to put the benefits provided by fuel additives into neat compartments as many of the benefits can be interpreted in different ways or help in more than one direction. However, they seem to fall naturally into four main areas:

- energy conservation
- air quality improvement
- cost saving during manufacture
- added value and quality to the user

6.3.1 Energy conservation

This falls into areas such as fuel production and fuel use.

At the refinery, the widespread use of flow improvers has arisen because of the economic pressures to use crude oil in the most effective manner, which means maximising the value and usefulness of each part of the barrel. Flow improvers have allowed refiners throughout the world, but particularly in Europe, to convert more of the low value heavy fuel oil into distillate fuel.

On the vehicle, cleanliness additives of all types help to improve fuel economy and reduce CO_2 emissions. There are numerous examples quoted in literature which show the improvements obtained from the use of deposit control additives for carburettors, port fuel injectors, diesel IDI and DI injectors, and inlet valves.

Cetane improvers also help to provide better diesel fuel economy.

6.3.2 Air quality improvement

The same detergent or cleanliness additives that improve fuel economy, also help to improve air quality by reducing CO, HC and CO_2 emissions. Again literature provides many examples of the importance of using additives to clean up carburettors (up to 48% CO decrease), inlet valves (up to 32% decrease in HC), gasoline port fuel and diesel injectors. The importance of maintaining clean injectors is demonstrated in many tests. Figure 27 shows the impact of clean-up on hydrocarbons, carbon monoxide and fuel economy from two passenger cars.

Use of cetane improvers also shows benefits in reduction of emissions of gaseous hydrocarbons (up to 45%) and particulates (around 50%) including the oil soluble fraction and products of specific concern such as fluoranthene.

The use of lubricity additives has made it possible for low sulfur environmentally friendly fuels to be marketed satisfactorily by meeting specification requirements for lubricity and provided needed fuel pump protection. The availability of antistatic additives also enhanced the safety aspects of distributing these fuels under all conditions.

The availability of anti-exhaust valve seat recession additives allowed legislators more freedom in their phaseout of leaded gasoline and helped to prevent engine failures, particularly in specialised equipment and the off-highway market.

6.3.3 Cost saving during manufacture

Most of the additives offer economic benefits to the refinery relative to alternative processing or blending options, or as ways of helping to maintain product quality until the product is used. Additives in this category include flow improvers, wax anti-settling additives, pipeline drag reduction additives, demulsifiers, corrosion inhibitors, antioxidants, metal deactivators, and stabilizers. In some cases such as military use, it is vital to maintain high quality fuels for very long periods.

6.3.4 Added value and quality to the user

The motor industry has welcomed the development of improved fuel additives and, through the World-Wide Fuel Charter (2) is pushing for improved quality as demonstrated by performance tests. The availability of additives has allowed the engine designers to use tighter standards of tolerance, as they develop lower emission engines, with the confidence that these performance levels can be maintained.

All new additives must be designed with exhaust catalyst compatibility in mind. As some governments are providing fiscal incentives for the use of alternative fuels, the motor industry also looks to the additive industry to help make these new fuels compatible with vehicle hardware.

The vehicle driver gets recognisable benefits from fuel additives. Deposit control additives have helped to maintain vehicle driveability. Antifoam additives have helped to promote the popularity of diesel engines for the passenger car market. Lubricity and anti-wear additives contribute to longer engine and other vehicle component life. While fuel economy is difficult for the private motorist to measure accurately, the benefits to the individual pocket and world energy conservation are both real and substantial.

7. Conclusions

Though dating back to the 1920s, the use of automotive fuel additives has only become widespread over the last decades. As the market continues to mature, driven by the needs of the fuel and vehicle industries and response to developing environmental pressures, this paper explains in some detail the chemical products which make up fuel additives and how they work. An attempt has also been made to define the size of the market.

Fuel additives end their life as combustion products which are emitted to the air compartment of the environment. But the contribution they make to regulated emissions is very small, and is outweighed many times over by the major vehicle emission reductions which could not have been made over the last few years without their help. Additionally their use brings other major environmental benefits in energy conservation, reduced maintenance, and economic benefits to both refiners and motorist.

In any overall environmental balance it is ATC's belief that the benefits clearly and significantly outweigh any risks attendant on their use.

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