Fuel Additives:
Use and Benefits

SEPTEMBER 2013 / ATC DOCUMENT 113

ATC
A SECTOR GROUP OF cefic
Technical Committee of Petroleum Additive Manufacturers in Europe

Contents

Abstract

The Technical Committee of Petroleum Additive Manufacturers in Europe (ATC) has produced this document which describes the chemistry and functions of fuel additives, as well as their role in the development of advanced engine and fuel systems. Product health and safety aspects are also reviewed.

This document supersedes Document 52 which was originally published in 1994. That first edition was written to provide information which was not previously available, with the purpose of putting in perspective the benefits to the environment and the end-user provided by fuel additive technology. This document updates the information and reanalyses the data.

In addition, information regarding the size and nature of the fuel additives market in the 27 countries of the European Community (EU-27) is provided.

Executive Summary

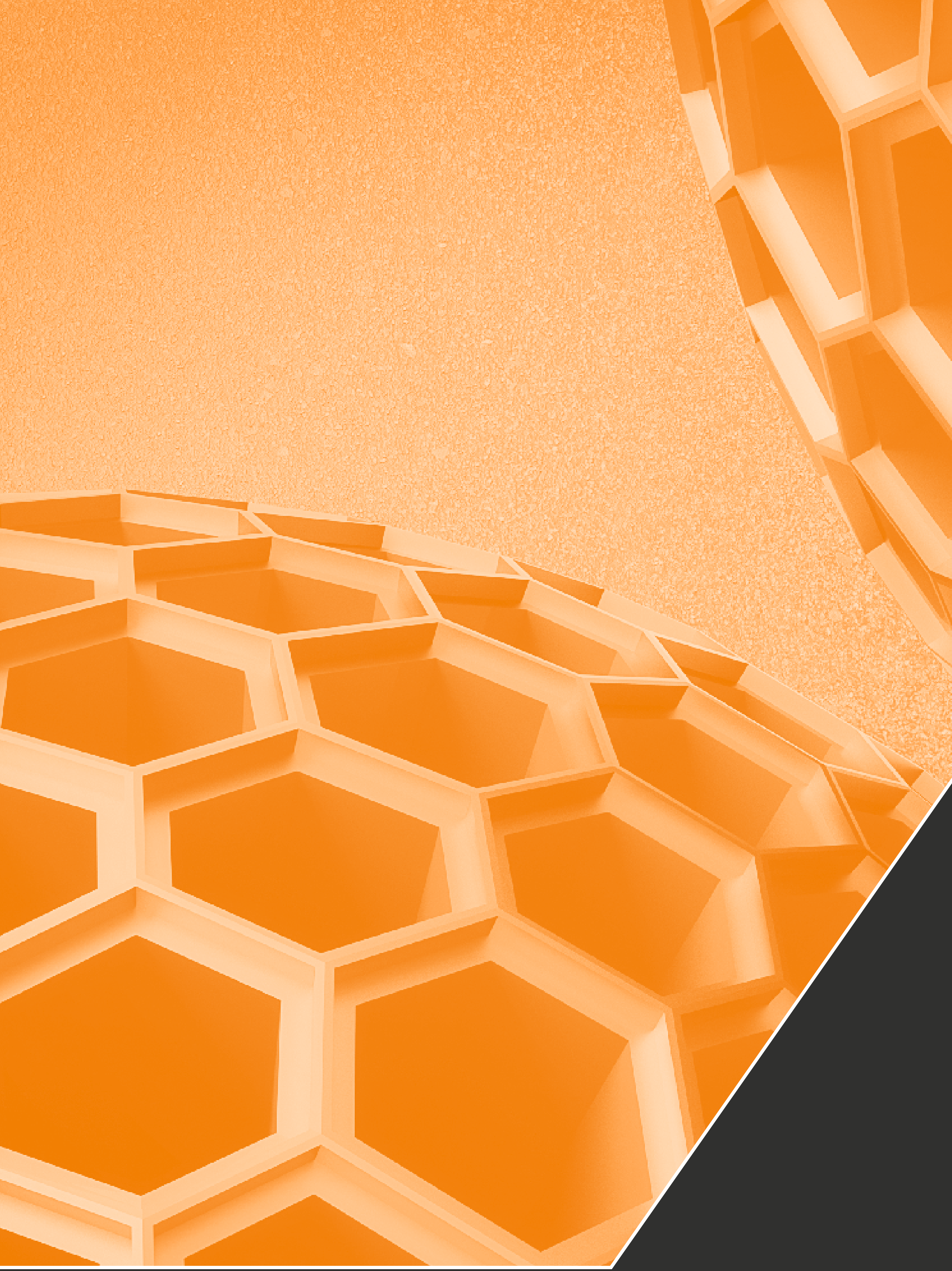
"Fuel Additives: Use and Benefits" is a document published by ATC, the Technical Committee of Petroleum Additive Manufacturers in Europe. Member companies of this body currently comprise thirteen speciality chemical manufacturers, including some household names, which together are responsible for the production and supply of almost all the additives used in fuels. Such additives encompass applications for gasoline (petrol) and diesel used for on and off road vehicles and machines, together with use in aviation, marine, power generation and home heating fuels. The document demonstrates the contribution made by fuel additives in these applications to the consumer, industry and the environment, through their ability to optimise desirable fuel properties while suppressing unwanted ones. In this context, the term 'fuel additive' is reserved for a product added to fuel at a concentration of typically less than one per-cent.

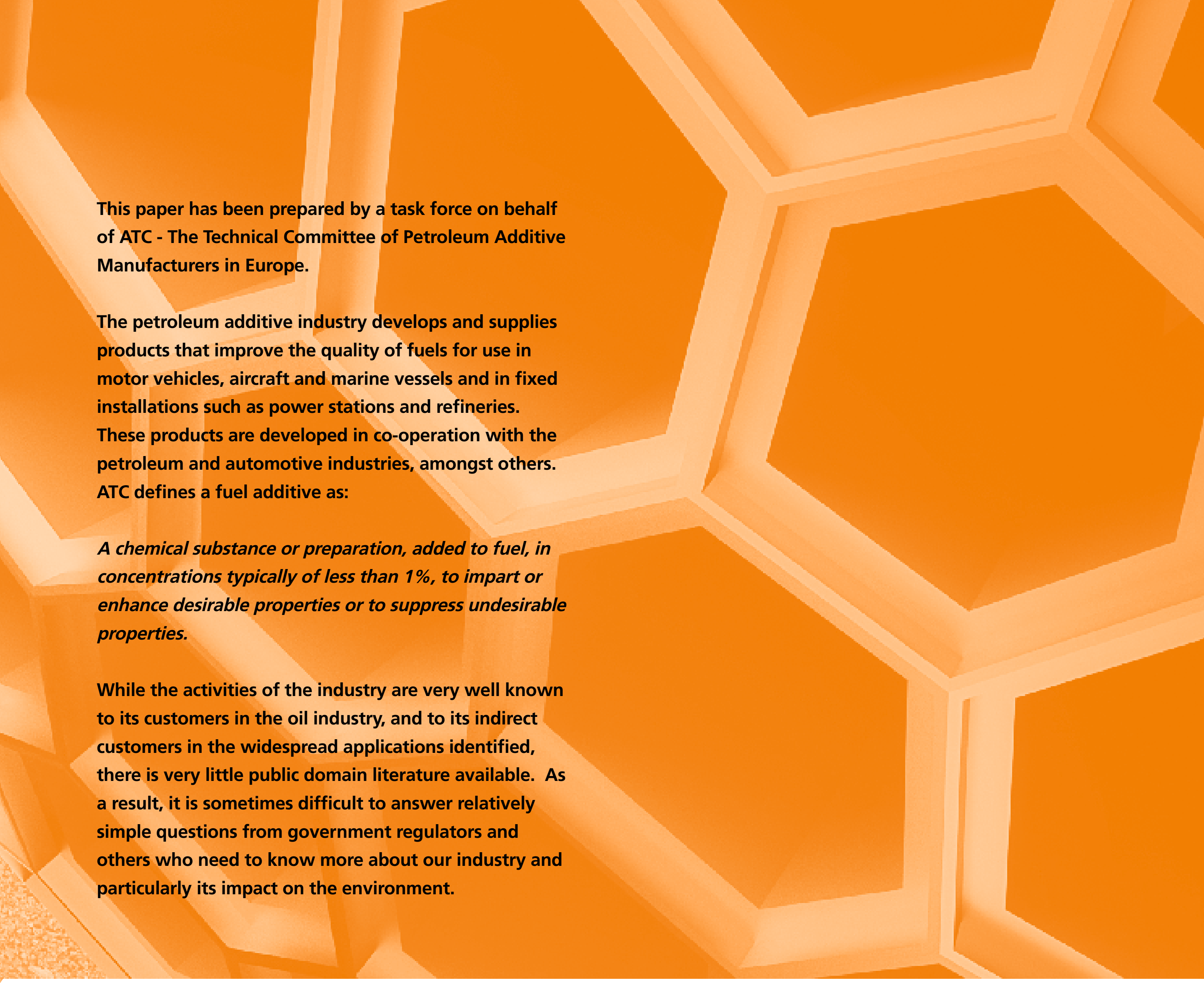
The structure and organisation of ATC provides for direction from a main committee through working-group sub-committees, which are responsible for performance testing, quality monitoring and health and safety legislation. The aim of ATC activities is to ensure good communication with industry bodies, together with active participation in appropriate technical development and product quality demonstration, to enable current and future products to contribute to optimised fuels and lubricants, meet environmental legislation, and/or resolve potential engine or vehicle problems.

The petroleum additive industry is a significant operating sector of the world economy, with a world-wide turnover of about €7,000 million, (€1,900 million in Europe) and research and development (R&D) spending in 2005 of €400 million (€115 million in Europe). The industry has 8,400 direct employees world-wide (2,800 in Europe), maintaining some 75 R&D and manufacturing sites globally (25 in Europe).

Innovation through R&D remains a constant in an industry based on change, to meet, for example the demands of environmental legislation with consequent effect on fuel specifications. Such activities have significant cost implications, as does the need to comply with European REACH regulations linked to health and safety legislation. Meeting these demands poses a significant challenge for the fuel and lubricants additives industry, a challenge which nevertheless the industry has shown it can meet since its infancy in the 1920s when lead alkyl anti-knock additives first proved to be very effective in lifting the very low octane quality of available spark-ignition fuels. Further developments have occurred in almost every decade, for example, additives evolved in the 1930s to enhance fuel stability in response to refinery changes to increase gasoline or middle distillate production, or the evolution of deposit control additives which provide performance gains in automotive fuel systems in the 1950s and 1960s. In a further example, a major improvement in diesel fuel cold weather behaviour and properties resulted from the development of cold-flow improver additives during the 1970s. More recent developments include diesel lubricity additives and fuel borne catalyst products for use with diesel exhaust particulate filters. With the increased use within the European Union of renewable blending components such as bio-ethanol in gasoline, and Fatty Acid Methyl Ester (FAME) in diesel fuel, there exists a future demand for novel additive products to ensure consistent high quality fuel production, and satisfactory vehicle operation.

"Fuel Additives: Use and Benefits" details a wide range of additives employed in refineries, automotive fuels and those for aviation, marine and also for fixed installation use. The document includes a systematic description of the chemistry of each additive, its purpose and its mode of action in its selected application. A section is devoted to the benefits of fuel additives both to the environment and the consumer, covering for example, fuel economy and exhaust emissions. In addition, consideration is given to the health and safety aspects of additive production and use, and also to the ultimate fate of fuel additives following the combustion process. The technical aspects of fuel additives are well covered, with over sixty references cited, thus providing an excellent basis for further study by those interested in increasing their understanding of this important branch of science. In addition, an appendix provides information about industry-standard test methods used for fuel additive performance assessment.





This paper has been prepared by a task force on behalf of ATC - The Technical Committee of Petroleum Additive Manufacturers in Europe.

The petroleum additive industry develops and supplies products that improve the quality of fuels for use in motor vehicles, aircraft and marine vessels and in fixed installations such as power stations and refineries. These products are developed in co-operation with the petroleum and automotive industries, amongst others. ATC defines a fuel additive as:

A chemical substance or preparation, added to fuel, in concentrations typically of less than 1%, to impart or enhance desirable properties or to suppress undesirable properties.

While the activities of the industry are very well known to its customers in the oil industry, and to its indirect customers in the widespread applications identified, there is very little public domain literature available. As a result, it is sometimes difficult to answer relatively simple questions from government regulators and others who need to know more about our industry and particularly its impact on the environment.

Introduction

Introduction

Aim

The aim of this paper is to introduce ATC, to explain how the association operates, and to demonstrate the contribution that fuel additives make towards industry, the consumer, and ultimately the environment. By answering questions, and providing additional data, the paper hopes to allow industry and regulators to focus on the priorities for future attention rather than matters which are trivial or already well known. These issues are principally covered in the sections "Benefits of Fuel Additives to the Environment and Consumer" and "The Ultimate Fate of Fuel Additives".

Scope

The document confines itself to a study of fuel additives, their chemistry, the benefits they provide and their fate in the environment. Fuel additives comprise those used in transportation fuels such as gasoline (petrol), diesel, aviation and marine fuels and those used in fuels employed for power generation and domestic heating. The study is based mainly on the 27 European Community members (as of December 2007). This choice was based on the availability of the widest range of data to allow cross checking for consistency.

ATC

The Technical Committee of Petroleum Additive Manufacturers in Europe (ATC) was established in 1974 for member companies to discuss topics of a technical and statutory nature which were a concern to their industry. The current members are shown in Table 1 below.

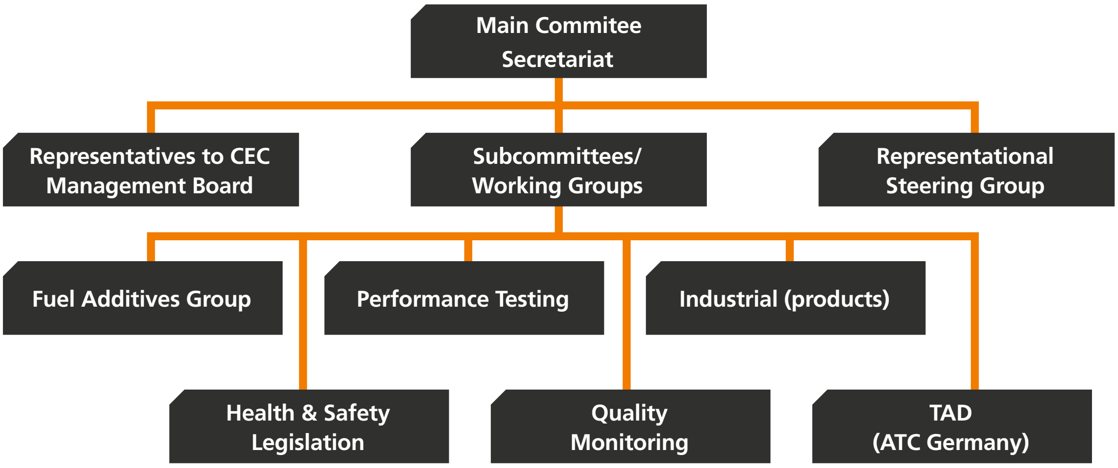
Table 1 - Members of ATC

Afton Chemical	Evonik RohMax Additives GmbH
Baker Hughes	Infineum
BASF	Innospec Fuel Specialties
Chemtura Corp.	Lubrizol
Chevron Oronite	Rhein-Chemie
Clariant	Total ACS
Croda	

Further information about ATC can be found on the website www.atc-europe.org. Membership is open to all additive companies which operate chemical processes for the manufacture of petroleum additives, or have comprehensive test facilities, in Europe. In 1979, ATC became affiliated as an industry sector group of Cefic, a federation of associations representing European chemical manufacturers.

ATC organisation and objectives

The ATC organisation is shown in Figure 1 below:



The ATC organisation comprises a main committee and sub-committees responsible for, amongst others, Health and Safety Legislation, Lubricant Performance Testing, Fuels Additives and Quality Monitoring.

ATC aims to provide a forum for petroleum additive companies in Europe to discuss technical and/or regulatory matters:

- to ensure that communications with appropriate international industry bodies are properly coordinated
- to participate actively in any technical work essential for the protection of industry interests
- to participate actively in CEC to ensure that products and technologies are seen as 'fit for purpose'
- to collaborate with the petroleum and automotive industries to allow development of products and technologies that contribute towards:
  - optimum provision of service fluids, fuels and lubricants
  - cost-effective compliance with present and future environmental legislation
  - resolution of identified or anticipated vehicle or engine problems

For example, ATC has developed descriptive terminology for products to assist legislators by providing standardised industry reporting whilst protecting confidentiality.[1] Technical data are shared to provide accurate labelling of products where required. More recently ATC has actively participated in discussions on aspects of environmental legislation including REACH (Registration Evaluation and Authorisation of Chemicals).

By communicating with associated industries and their technical bodies (e.g. ACEA - Association des Constructeurs Européens d'Automobiles; CEC - Coordinating European Council for the Development of Performance Tests for Lubricants and Engine Fuels; ATIEL - Association Technique de l'Industrie Européenne des Lubrifiants; CONCAWE - The Oil Companies' European Organisation for Environmental and Health Protection) technical issues can be addressed in an agreed and consistent manner and recommendations can be made to the mutual interest of the members. ATC also provides a focal point for the industry to communicate with government bodies.

Introduction

The petroleum additive industry

The petroleum additive industry is a research and development intensive industry and its products are marketed almost exclusively to industrial users.

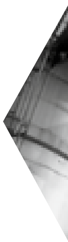
ATC estimates, from data submitted through member companies, that the EU27 market for fuel additives is over 200,000 tonnes per annum with a value of €500 million. ATC further estimates that over 95% of on road retail fuel (gasoline and diesel) is treated with performance additives, accounting for approximately half of the volume, with the remainder being sold into refineries and terminals to ensure fuels are produced to specification (EN590 & EN228). All European refineries use additives in some capacity.

The fuel additive business

A very wide range of additives has been developed to meet the needs of an industry which converts principally hydrocarbon fuels into heat energy, either to provide transportation or to generate electricity for industrial and domestic consumption. The wide range of products required reflects both the range of fuel types that benefit from additive use and also the range of performance features that can be improved, or operational problems that can be overcome, through the use of additives. These may be encountered at the refinery, in distribution systems and storage tanks or in use, for example, in numerous different transport applications. An additive may be used as a single stand-alone product to resolve a specific issue, for example at the refinery or, frequently, may be combined with other products to create a multi-functional package for use in finished fuels for the automotive industry. Fuel additive treat levels are generally low, with some additives dosed at single figure mg/kg (ppm) levels. Others are employed at treat levels ranging from 50-500 mg/kg, while a multifunctional package may be used at treat levels in the range 350-3500 mg/kg (0.035-0.35 %) depending on the extent and range of benefits desired. Additive treat levels employed do not approach those of fuel blending components (such as ethanol for use in gasoline, or fatty acid methyl esters (FAME) in diesel fuel), where use levels are typically 3-20 % of the hydrocarbon base fuel volume.

Development of new additives

Innovation is an on-going requirement in the fuel additives business, often driven by legislation which changes the specification of fuels (not only automotive fuels) or demands the use of higher quality fuels. Reduction of sulphur content in middle distillate fuels, for example, has led to the need to develop lubricity additives to protect diesel injector pumps. In another instance, there may be the need to develop a new and enhanced multi-functional additive package (possibly including novel additive components) to enable vehicle fuel economy to be improved while minimising the emission of regulated exhaust pollutants. Growth in the demand for diesel exhaust particulate filters, for example, has spurred the development of fuel borne catalyst additive products to assist on-board filter cleaning, or regeneration, of the particulate filter.



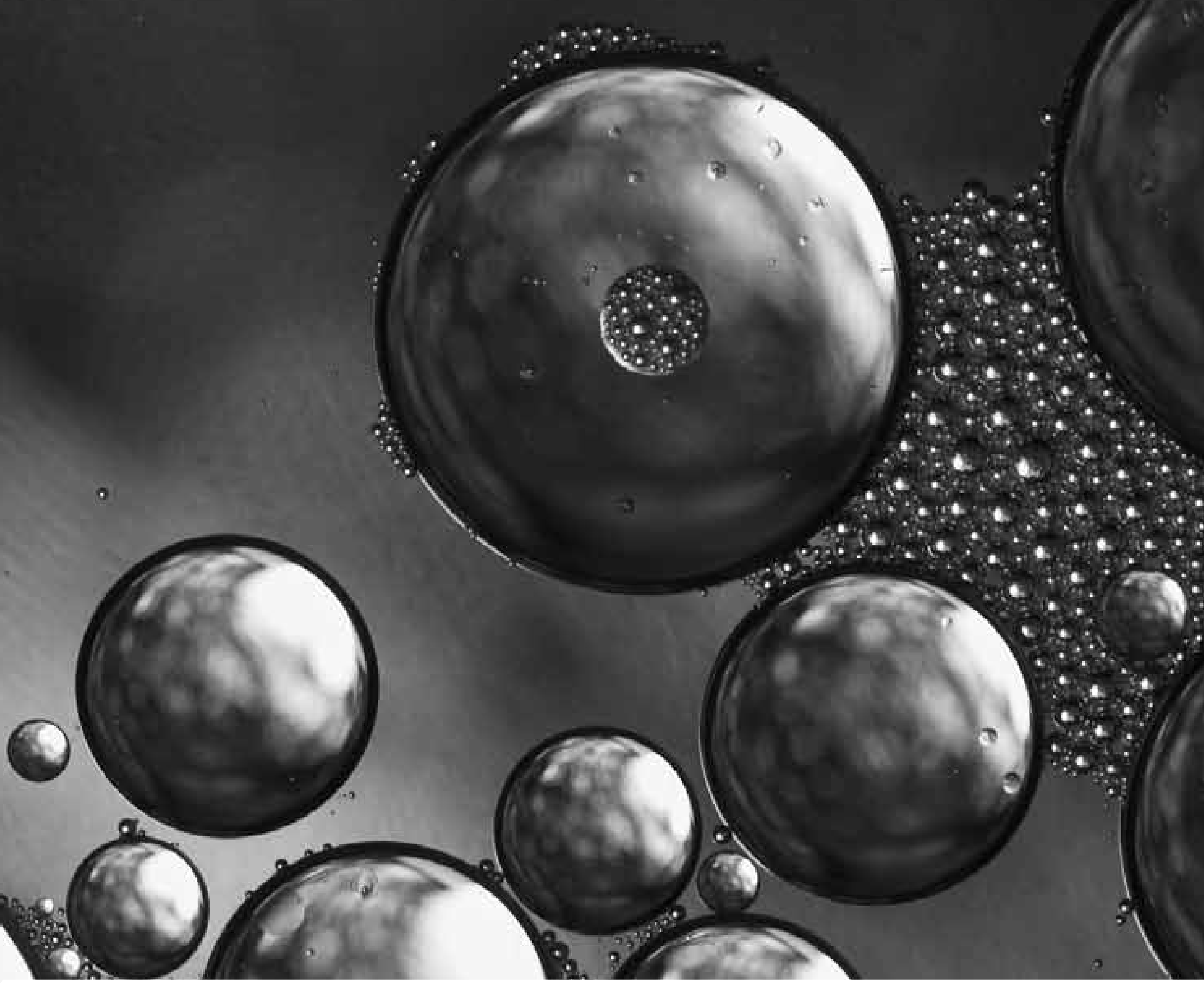
Cost complexity and confidentiality

The development of new fuel additives to satisfy the demands of current and future fuels incurs significant costs. Expensive engine testing or vehicle demonstration trials are often needed and, invariably, a considerable number of laboratory tests are necessary to produce the required suite of supporting data to enable supportable performance claims to be made. In addition, the cost of compliance with health and safety legislation has risen over the years and will increase still further with the implementation of REACH regulations.

A lack of innovation could have serious consequences. Today's engines will not function optimally on yesterday's fuels. Tomorrow's engines will need new additive developments. With the continuing quest for cleaner and more fuel efficient engines, engine developments are proceeding rapidly, yet engine manufacturers recognise that fuel additive developments must accompany and support these improvements if the enhanced performance is to be maintained over the life of the vehicle.

Patents, for various reasons offer only limited protection - one being the difficulty of policing due to problems of analysis. Combinations of components in an additive package to achieve the required performance may not be readily patentable, therefore many such inventions are treated as proprietary compositions (company secrets) without additional patent protection.

To ensure continued innovation and investment in R & D to meet the needs of the automotive industry and the consumer, the additive industry requires confidentiality of the exact chemical descriptions of components and exact composition of additive packages. To satisfy both this requirement and the current legislative requirement for disclosure of hazardous ingredients on Safety Data Sheets (SDS), ATC has established an international nomenclature system describing chemical ingredients in terms of their key functional groups.[1] This system ensures that accurate and unambiguous health and safety information on all products can be provided which is recognised by industry downstream users and emergency personnel worldwide.[2] This nomenclature system is also used by international regulatory bodies.



History Of Additive Development

HISTORY OF ADDITIVE DEVELOPMENT

The pre-additive period – until 1921

In the early days of gasoline production, broadly from the end of the 19th century, fuel for spark ignition engines was essentially a waste product. Furthermore there was almost no demand for fuels for compression ignition engines, and lighter middle distillate fuels were mainly used for illumination or in cooking stoves. Consequently there was no incentive to produce fuel additives until well into the 20th century. As more gasoline engines were produced for automotive use, the low octane quality of the straight run light distillate product used in spark ignition engines began to represent an increasing barrier to engine development.

The main steps of fuel additive development – 1920s to the present

Major developments in gasoline additive use

The growth in gasoline additive use largely reflects the requirements of engine design and developments in refinery operations. For example, after the discovery of the effectiveness of lead alkyl antiknock compounds in 1921,[3] these additives began to be commercially introduced from 1923 onwards to provide the octane rating needed to enable vehicle designers to increase engine compression ratios to levels which gave acceptable efficiency and performance. Increasing demand for gasoline from a rapidly rising vehicle population resulted in the increasing use of cracking operations at refineries. However, inclusion of cracked spirit into the gasoline pool introduced side effects. Antioxidants were introduced in the 1930s to combat the tendency of cracked components to oxidise and form gums.[4] These products became significantly more important in the 1970s when further increased use of catalytic cracking, to satisfy ever higher demand for gasoline and diesel production, raised the levels of unstable olefinic (unsaturated) compounds in these fuels.

The focus of additive use shifted during the 1950s and 1960s and fixed on automotive fuel systems, when carburettor cleanliness and efficient operation became more important. During the 1980s, deposit control additives were increasingly used to reduce deposit build-up within the engine inlet system and to eliminate the potential performance and emissions problems such deposits can cause.[5] The almost universal elimination of lead alkyl additives from gasoline around the turn of the last century resulted in the development of additives to protect against unwanted exhaust valve seat wear in older engines constructed with unsuitable metallurgy.[6] Fuel metering technology has moved on, with the result that different additives and additive packages have been developed. The now universal use of three-way exhaust catalysts and fuel injection has shifted the focus again, but has retained the need to keep such fuel systems deposit free.

Comprehensive deposit control additive packages are now widely used, and recommended by vehicle manufacturers, as a means to maintain optimal engine performance.[7] The incorporation of biofuels, such as ethanol, into the gasoline pool could increase the potential for deposit formation and, consequently, higher additive levels may be required. With the current increasing pressure to reduce carbon footprint to a minimum, such packages may also contain components intended to minimise fuel consumption, in addition to those intended to maintain fuel system cleanliness.

Major developments in diesel additive use

As with gasoline additives, diesel additive use reflects the impact of growing diesel fuel demand and the changing technology of diesel engines. In the early days of diesel engine development, cold starting and ignition quality were major development issues. One of the earliest diesel fuel additives employed during the 1920s was an ignition improver still in use today, which greatly assisted in overcoming these problems. Its use, coupled with the low specific fuel consumption of the diesel engine, assisted in the widespread adoption of the diesel engine as the power unit for heavy goods vehicles and locomotives.

Demand for diesel fuel increased rapidly and placed heavy burdens on refinery production.[8] The introduction of wax crystal modifiers (cold flow improvers) during the 1970s was critical to increasing diesel fuel availability. Without these additives, it is likely that the performance of diesel vehicles could not have been maintained during the winter months without additional cost to refineries, or the use of more complex and expensive vehicle fuel systems.

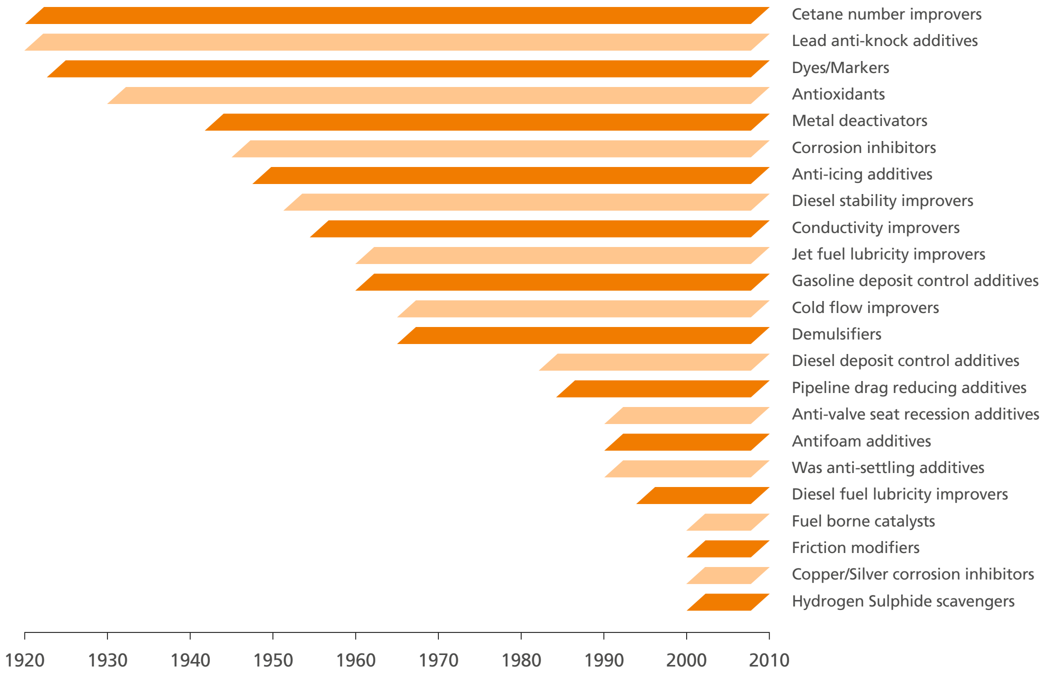
The changing pattern of refining in the late 1970s / early 1980s also had an impact on diesel fuel quality. The need to use a greater proportion of the crude barrel to produce increased volumes of middle distillates resulted in cycle oils from catalytic crackers being blended into diesel fuel. Cracked material has a lower cetane quality than straight-run distillate components. Cetane number is the metric for diesel fuel ignition quality, thus the use of cetane number improver additive was necessary to meet the refinery cetane specification and to provide fuels with the required ignition quality. Meanwhile, diesel engine manufacturers and operators had become convinced of the benefits of high cetane quality diesel fuels, again resulting in the increased use of cetane number improver additive. The tradition of high cetane quality diesel fuels has been maintained in Europe for decades, with the result that cetane improver additive is a widely used and cost effective product.

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 reinforced the need for deposit control additives to keep the engine clean and maintain long-term vehicle emissions performance. The introduction of very low sulphur fuels led to a need for lubricity additives, increased the requirement for conductivity improver additives and created a need for revised or novel additives to improve oxidation stability. Conversely, the use of Fatty Acid Methyl Ester (FAME) as a renewable diesel blending component has reversed or reduced the need for lubricity and conductivity improvers whilst making the oxidation stability situation more complex.

Fuel additive types and history

An indication of the approximate dates of introduction of major fuel additive types is given in Figure 2 below.

After introduction, many additive types continue to evolve to meet the changing technical and performance requirements of the market.



History Of Additive Development

Main additive component families

Additives can be sub-divided in terms of their point of application as indicated below:

- Refinery products
  - Antioxidant and stability improver additives
  - Octane/cetane enhancing additives
  - Cold flow improver additives
  - Metal deactivator additives
  - Dyes
- Distribution system products
  - Corrosion inhibitors
  - Pipeline drag reducing additives
  - Anti-static additives
- Automotive performance enhancement products
  - Deposit control additives
  - Cetane improvers
  - Lubricity additives
  - Friction modifiers
  - Antifoam additives
  - Corrosion inhibitors
  - Demulsifiers/dehazers
  - Anti-valve seat recession additives
  - Fuel borne catalysts for particulate filters

Multi-Functional Additives

Combined packages of a number of selected additive components can be assembled to provide a bespoke performance-enhancing additive for use by fuel retailers for their products. Such packages enable retailers to differentiate their automotive fuel products at the point of sale to the consumer. They allow increased performance features to be highlighted, and provide a means to sell a higher quality product to the discerning customer at increased margins. They also represent a cost effective and efficient way of delivering multiple benefits conveniently in a single additive treatment at the fuel terminal or pipeline, prior to delivery to the customer sales outlet.

Multifunctional gasoline additive packages will often combine a deposit control additive with a corrosion inhibitor and demulsifier additive. Multifunctional diesel additive packages are frequently more complex and may combine deposit control additive with cetane number improver, antifoam additive, corrosion inhibitor and demulsifier (and possibly also cold flow improver additives depending on seasonality).

The composition of multi-functional diesel additives is influenced by national and regional legislation, as well as consumer demands and perception. For example, silicon (Si) based antifoam additives are widely used in European diesel fuel but are not used in the United States due to legislation that prohibits the addition of Si to fuel. Fuel additisation can also be influenced by governments who regulate the cost of fuel and provide allowances for a premium to be charged for additised fuels.

The Role of Fuel Additives in the Vehicle

The Role of Fuel Additives in the Vehicle

Vehicle hardware/OEM trends

The middle decades of the 20th century witnessed a general stagnation in vehicle design, with the main emphasis on reducing initial purchase cost. Since the mid-1970s in the USA and the mid-1980s in Europe however, air quality concerns led to the gradual phasing out of tetra-ethyl lead antiknock additives in gasoline and the reduction of sulphur levels in diesel fuels. Consequent upon these general trends, the demands placed on vehicle manufacturers can be summarised as follows:

- reduced exhaust pollutant levels
- increased specific power output
- increased fuel efficiency
- increased service interval duration
- greater reliability

Some of these demands are conflicting yet, in large measure, have been met. Fuel additives have played a valuable role in assisting Original Equipment Manufacturers (OEMs) to meet these challenging demands, to the extent that OEMs now recognise the value, and recommend the use of, fuel additives in assisting them to meet such requirements. The development of new fuel injection systems, such as high pressure common-rail diesel injection or gasoline direct injection has created further demand for novel products to ensure optimal, long term operation in service.

Ensuring “no-harm” for fuel additives

The fuel additive industry has long recognised the need to ensure that in resolving one issue, the use of a fuel additive does not create another. Products have only received endorsement, or had their use encouraged, if refiners and OEMs have been satisfied that no harmful (in service) effects will result from the use of fuel additives. This is typically accomplished by performing extensive laboratory and/or engine tests and has resulted in the creation of a “no-harm” suite of tests, performed to demonstrate the absence of adverse effects of fuel additive use.

Awareness of the need for such tests comes from effective dialogue and collaboration between oil refiners and retailers, the fuel additive industry and vehicle and engine manufacturers. When problems are noted in service, test methods are developed to simulate the problem, enabling fuel additives to be tested to an agreed performance level before the product is released for sale. Examples of this process below demonstrate how fuel additives and test methods have evolved to overcome issues of unwanted adverse side effects in the past.

Intake valve sticking

Some gasoline deposit control additives were found to permit the formation, at the intake valve stem/guide interface, of a film whose viscosity increased very significantly at low ambient temperatures. Under these conditions, on cold cranking immediately prior to start-up, one or more intake valves could stay open, with the compressed valve spring unable to close the valve in time to allow cylinder pressures to rise satisfactorily, with engine cold starting and operation potentially severely compromised as a result.[9] The additive industry responded by developing a specific test procedure using an engine noted to be particularly (and severely) affected by the problem. This test procedure is now a standard no-harm test for multifunctional gasoline additive packages.

Lubricating oil interaction

Some lubricity additives used in low sulphur diesel fuels were found to react adversely to contact with crankcase lubricating oil.[10] The potential for contact between crankcase lubricating oil and diesel fuel occurs in some in-line injector pumps used on many heavy duty diesel engines. Where problems occurred, deposits in the pump plunger region could seriously impair pump operation, with resulting loss of engine power output or possibly complete shutdown. The fuel and additive industry rose to this challenge by developing laboratory interaction tests involving both new, and used, crankcase lubricating oil and candidate lubricity additive chemistries, to ensure that no deposits would occur in service. Such tests have now become standard no-harm tests for diesel fuel packages containing lubricity additive.

Chemistry of Gasoline Fuel Additives

CHEMISTRY OF GASOLINE FUEL ADDITIVES

Deposit Control Additives

Intake system components

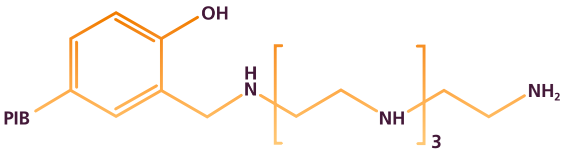
Deposit Control Additives (DCAs) consist of a polar head, the polarity of which is derived from oxygen or nitrogen molecules and a hydrocarbon tail which enables the additive to be fully fuel soluble.

Examples of molecules that are used include amides, amines, polybutene succinimides, polyether amines, polyolefin amines and Mannich amines. Poly isobutene (PIB) is widely used as the hydrocarbon tail due to its reactivity during processing, excellent solubility in fuel and the thermal stability it imparts to the completed molecule.

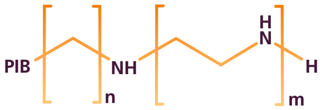
Deposit Control Additives are often referred to by the generic term **detergents** but their function is different to that of conventional detergents used for washing and cleaning purposes. Conventional detergents are controlled by European Regulation (EC) 648/2004 (the 'Detergents Regulation'), which provides protection of the aquatic environment from pollution by detergents used for washing and cleaning. Chemically, DCA are similar to **dispersants** used in lubricants and have been deemed by the European Commission to fall outside the scope of the Detergents Regulation.[11]

Examples of Gasoline DCA

PIB Phenol Mannich Amine



PIB Amine



Purpose

Deposit Control Additives are designed to keep the entire engine fuel system clean, from the fuel tank to the combustion chamber.[12,13,14,15,16,17,18,19] They prevent the formation of deposits, particularly on intake valve and fuel injectors, that derive from the breakdown of gasoline components. These deposits would otherwise deteriorate the air and fuel flow through the engine, reducing performance, efficiency and increasing emissions.

Mode of Action

Deposit Control Additives inhibit deposit creation by forming protective films which prevent deposit precursors accumulating to form deposits. They operate at the temperatures and pressures experienced within the engine where the cleaning process is a function of temperature, air/fuel flow and physical mechanisms. Deposit control additives are intended to be used on a continuous basis to avoid deposit build-up but, by changing the equilibrium between the accumulation and removal mechanisms, they can also provide a deposit removal function. They operate throughout the fuel system of the engine, wherever the fuel is in liquid form but, with the appropriate chemistry and treat rate, can also reduce deposits within the combustion chamber.

It is normal to combine gasoline Deposit Control Additives with fluidisers / carrier oil molecules (see below) to avoid build-up of deposits on valve stems that can lead to valve-stick and poor engine starting.

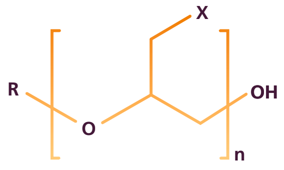
Fluidisers / Carrier Oils

Fluidisers or Carrier Oils are thermally stable structures such as Poly-Alpha-Olefins, Poly-Ethers, Poly-Glycols or heavy esters (Mw ~1000-2000). Synthetic polyether derivatives such as Poly-Propylene-Glycols and Poly-Butylene-Glycols are also commonly used.

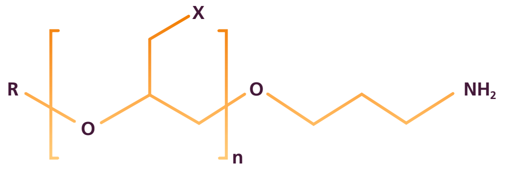
Carrier Oils are used in combination with, and at a treat rate 0.5 to 3 times that of, the DCA to form the full deposit control package. In the case of Poly-Ether-Amines, the carrier oil function is 'incorporated' within the DCA structure and therefore requires no additional carrier oil to be used.

Example of Fluidiser

Alkyl polyalkylene glycol ether
(R = C_{12}, X = H, CH_3)



Alkyl polyalkylene glycol etheramine
(R = C_{12}, X = H, CH_3)



Purpose

High viscosity deposits can form at the intake valve stem/guide interface of an engine during cold weather. Under these conditions, on cold cranking immediately prior to start-up, one or more intake valves could stay open, with the compressed valve spring unable to close the valve in time to allow cylinder pressures to rise satisfactorily, with engine cold starting and operation potentially severely compromised as a result. Carrier fluids are used to ensure that engines are not prevented from starting even during extreme cold weather.

Mode of Action

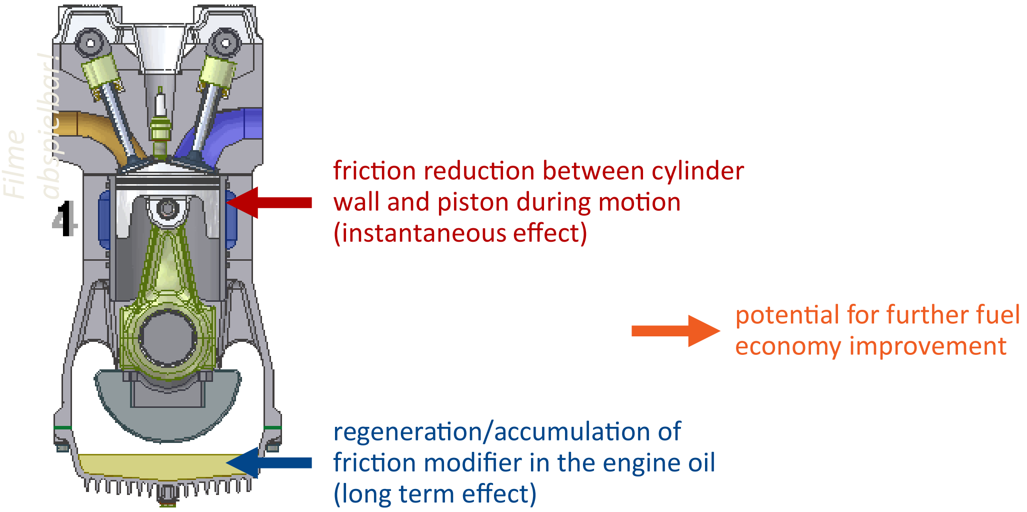
Carrier oils, as part of a DCA package, help the DCA component to both prevent deposit formation and ensure no valve sticking occurs. Intended to form a thin film on surfaces, carrier oils ensure that partially combusted particles can run off the hot metal surface of inlet valves. They can accomplish this as carrier oils in DCA packages possess high thermal stability, an optimised viscosity and excellent compatibility with both fuels and lubricants. Typical treat rates of the combined DCA / carrier oil package are in the range 100 - 1000 mg/kg.

Friction Modifiers

Friction modifier (FM) additives are well known and widely used in crankcase lubricant additive packages. They are generally straight hydrocarbon chains with a polar head group. Typical polar head groups comprise amines, amides and their derivatives or carboxylic acids and their derivatives. The polar head groups are attracted to metal surfaces such as cylinder walls and piston ring wiping faces, where they form relatively strong bonds, while the long hydrocarbon tail remains solubilised in the film of lubricating oil. The nature of the polar head group and the structure of the hydrocarbon chain both have a strong impact on the contribution to friction reduction.

Friction Redution

How does a friction modifier work?



friction reduction between cylinder wall and piston during motion (instantaneous effect)

potential for further fuel economy improvement

regeneration/accumulation of friction modifier in the engine oil (long term effect)

Example of Friction Modifier

Glycerol Mono-Oleate

Chemistry of Gasoline Fuel Additives

Purpose

Friction modifier additives used in fuel are intended to reduce power loss from friction in internal combustion engines. Power loss results in part from the viscous drag of lubricant in the film separating the moving parts of the engine and FM additives help to reduce viscous drag while maintaining the essential boundary lubricant film.

Mode of Action

Friction modifier additives function through the attachment of the polar head group to metal surfaces nominally in contact with each other. Surfaces accessible to fuel borne FM additives consist mainly of cylinder walls and piston ring surfaces. Viscous drag in the lubricant film, resulting from the relative motion of these surfaces during engine operation, is reduced by assisting the metal surfaces to slide past each other more easily. The film of polar molecules adsorbed on the metal surfaces provides a lower shear region during relative motion. Film stability is assisted by the long hydrocarbon chain which remains solubilised in the lubricant film. Lower friction from reduced film drag can result in improved engine power and/or fuel economy. Typical treat rates are in the range 50 - 300 mg/kg.

Corrosion Inhibitors

Corrosion inhibitors consist typically of a polar head to enable adhesion to the metal surfaces to be protected, and a hydrocarbon tail to ensure fuel solubility.[4,5] Effective corrosion inhibitors include carboxylic acids, anhydrides, amines and amine salts of carboxylic acids.

Example of Corrosion Inhibitor

Dodecenyl Succinic Acid

Rusty / clean probes

Purpose

Water associated with gasoline, or which infiltrates from external sources, combines with air to attack iron and other metallic surfaces in both the fuel distribution and vehicle fuel systems. Corrosion of ferrous metals produces rust, while other metallic surfaces can also deteriorate in the absence of an effective corrosion inhibitor. Fuel system corrosion can have very serious effects, particularly with the widespread use of complex precision equipment such as fuel metering pumps and injectors. Rust from corrosion can also block fuel filters and lines. Protection from corrosion is therefore essential for the reliable operation and long life of fuel storage tanks, fuel distribution pipelines and vehicle fuel systems.

Mode of Action

The polar portion of the molecule adheres to the metal surface, forming the protective film required. The hydrocarbon tail allows the molecule to be solubilised in the fuel thus providing a delivery mechanism to protect vulnerable metal surfaces.
Corrosion inhibitors are applied either at the refinery, pumping station, terminal or as part of a multifunctional additive package. Treat rates are in the range 5-100 mg/kg.

Antioxidants

Antioxidant chemistry typically comprises hindered phenols, aromatic diamines or mixtures of alkyl phenols and aromatic diamines. Oxidation of fuel, also termed instability, leads to deterioration, resulting in fuel darkening and the formation of gums and sediments. Antioxidants enhance gasoline stability and inhibit its tendency to deteriorate in storage.[4,20]

Purpose

Gasoline can contain a number of unstable species such as olefins and dienes and these can polymerise to form gums. Gums in the fuel are transported through the fuel system and can lead to malfunction and breakdown. In the fuel system, gums can be responsible for injection system fouling and are implicated in intake valve deposit formation.

Mode of Action

Unstable species in gasoline produce free radicals which combine with oxygen to produce further free radicals in a chain reaction and react with olefinic compounds to form gums. Unchecked, this oxidative chain reaction increases at an exponential rate producing increasing amounts of free radical and/or peroxide species. Antioxidants work by disrupting the chain propagating steps, by decomposing peroxides and by acting as free radical traps. Hindered phenols, for example intercept free radicals to form stable hindered radicals which do not propagate further. Typical treat rates are in the range 8 - 100 mg/kg.

Conductivity Improvers

Conductivity Improvers (also known as anti-static additives) comprise either fuel-soluble chromium materials, proprietary combinations of polymeric sulphur and nitrogen compounds, quaternary ammonium salts or complex organic alcohols. These chemistries enhance fuel conductivity at extremely low fuel treatment levels and reduce the potential for static charge accumulation.[19]

Purpose

Static electricity can accumulate in fuel during pumping operations. The problem can occur at refineries, terminals or closer to the point of use at filling stations or airports and is exacerbated by physical effects such as pipeline diameter reductions and particularly by in-line filters. Static discharges present an obvious and proven fire hazard, which can be reduced by improving the electrical conductivity of the fuel and dissipating electrostatic charge. Additive use is much more commonplace in fuels of intermediate volatility such as aviation kerosene, but low sulphur gasoline and diesel fuels are increasingly also treated.

Mode of Action

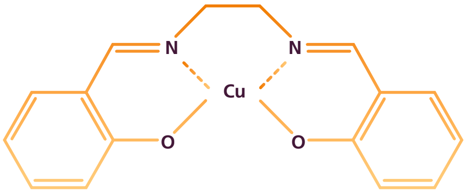
Conductivity Improvers greatly enhance the conductivity of the blended fuel, even at very low treat rates. With fuel conductivity above a critical threshold level, static charge accumulation from pumping operations cannot readily occur and charge dissipation rates are increased, thus preventing static discharge. Typical treat rates are in the range 1 - 40 mg/kg.

Metal Deactivators Molecule

The most commonly used metal deactivator additive (MDA) is N, N'-disalicylidene-1, 2-propanediamine, which has the ability to chelate or 'cage' dissolved metal ions. The presence of metals, particularly copper, in gasoline is associated with reduced oxidation stability .[4,20]

Example of Metal deactivator

N-N'-disalicylidene-1,2-propanediamine



Purpose

Soluble metal salts present in gasoline are known to promote instability in the fuel by catalysing the oxidation reactions, with subsequent gum formation and deposit build-up in the fuel system and on intake valves. Copper is particularly associated with instability in fuels; its presence in the form of a soluble salt even at very low levels can markedly reduce fuel stability resulting in the adverse effects described.

Mode of Action

Metal deactivator additive functions by reacting with dissolved metal in the fuel to form a stable chelate in which the metal has no pro-oxidant effect. N,N'-disalicylidene-1,2-propanediamine also migrates to new surfaces, inhibiting the formation of soluble metal salts. Typical treat rates are in the range 4 - 12 mg/kg.

Markers & Dyes

Colouration of gasoline is achieved by azo compounds and/or anthraquinone.[4] The chemistry involved with petroleum dyes is similar to that of other dye applications, but represents a rather specialised technology outside the main activity of ATC members.

Purpose

Markers and dyes are often employed for the purpose of differentiation between different commercial grades of gasoline and are also used to distinguish products attracting different duty levels, or to identify specialist products, e.g. aviation gasoline. Markers show no visible effect in fuel but on extraction with a solvent, will impart distinctive colours. Other markers can require UV or IR spectroscopy to reveal their presence and may comprise bio or nano-materials. These techniques can be useful in providing inventory control or in deterring theft.

Mode of Action

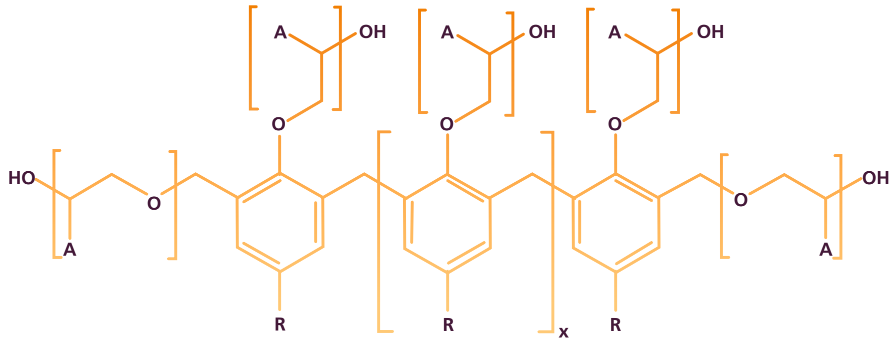
Markers and dyes are usually added at the refinery or in additive packages at the terminal to meet the specific requirement of the client. Typical treat rates are in the range 2 - 50 mg/kg.

Demulsifiers / Dehazers / Emulsion Preventatives

Demulsifiers are complex mixtures of a wide variety of alkoxylate chemistries including phenolic resins, esters, polyamines, sulphonates or alcohols which have been reacted with ethylene or propylene oxide. The products have oil **and** water soluble tails that allow them to migrate to the fuel / water droplet interfaces where they act.[5,20] They can be applied at refineries, fuel storage systems or contained within additive packages for finished fuels to break, or prevent, water based emulsions formed within fuels.

Example of Demulsifier

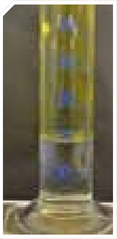
Phenolic resin alkoxylate



A=H or CH_3

Fuel / water emulsion

Separation of water from fuel



Full seperation

Purpose

Water contamination can be present in fuel anywhere in the distribution system from the refinery to the vehicle fuel tank. With agitation, particularly in the presence of other additives, water can become entrained in the form of a stable emulsion within the fuel. Problems associated with emulsions are blockage of fuel filters, promotion of microbial growth and corrosion. Hazy fuel appearance is also evident and this may reduce the value of fuel. Dehazers are emulsion breakers applied to fuels. These additives can be added to hazy fuel in storage to rapidly break otherwise stable emulsions and allow removal of the water from the fuel. Demulsifiers are emulsion breakers applied to lubricating and other oils. Emulsion preventatives are specifically designed to work with other performance package components to prevent the blended fuel and package formulation from forming emulsions with any water contacted within fuel distribution systems.

Mode of Action

These products modify the interfacial tension viscosity or film elasticity of water droplets within a fuel emulsion. This allows coalescence and separation of the water droplets from the fuel.

Dehazer and demulsifier dose rates for breaking existing emulsions are typically 10 – 500 mg/kg. Emulsion preventative dose rates are typically 1 – 10 mg/kg.

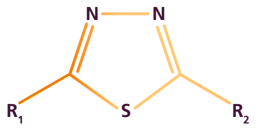
Chemistry of Gasoline Fuel Additives

Copper / Silver Corrosion

Additives to inhibit copper / silver corrosion in fuel systems frequently employ thiadiazole chemistry, while benzotriazoles have also been found to be effective.

Example of Copper/Silver Corrosion Inhibitor

Thiadiazole chemistry



Cu strip rainbow

Purpose

The presence of sulphur compounds in gasoline can have a corrosive effect upon non-ferrous metals. Copper corrosion tests have been used for many years to assess the potential effects of any sulphur compounds present but the increasing use of silver, or silver alloys, in the electronic sensors employed by modern automotive fuel systems has demonstrated their higher susceptibility to corrosion by low levels of sulphur compounds in the fuel. Production of low sulphur gasoline by refinery hydrotreatment paradoxically has exacerbated the problem by removing compounds which gave some natural protection against corrosion of silver contacts. Low sulphur gasoline is often treated at the refinery to prevent this type of corrosion.

Mode of Action

Copper / silver corrosion inhibitor additives act as film formers, creating a barrier over metal surfaces which prevents sulphur from reaching, and reacting with, the surface.

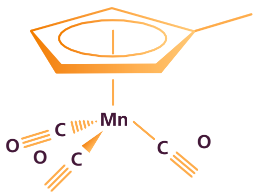
The addition of copper / silver corrosion inhibitor additives can be performed at the refinery or as part of a multifunctional package. Additive treat rates lie typically in the range 2-20 mg/kg.

Octane Boosters

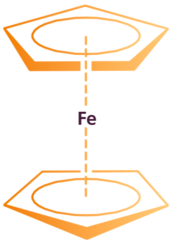
Octane boosters or antiknock compounds comprise, principally, organometallic chemistries including tetraethyl lead (TEL), ferrocene and methylcyclopentadienyl manganese tricarbonyl (MMT).[3,4,21,22] Organic compounds such as N-methyl aniline, ethanol, methyl tertiary butyl ether (MTBE), etc. are less effective than organometallic additives and are typically used at levels between 1% and 15%. They are considered blending components rather than octane boosters / antiknock compounds.

Examples of Octane Booster

MMT: Methylcyclopentadienyl Manganese Tricarbonyl



Ferrocene



Purpose

Octane boosters provide cost effective improvement in gasoline octane quality. Modern spark ignition engines have a typical octane requirement in the range 90-98 research octane number (RON). Operation on fuel of inadequate octane quality produces unwanted noise from detonation and may result in engine damage. The use of octane booster additives is now greatly diminished following refinery reconfiguration to produce naturally high octane blending components for the gasoline pool. Lead alkyl additives are still employed in aviation gasoline and at a very small number of refineries which lack the necessary processing capability to produce adequate octane quality. MMT, and to a lesser extent ferrocene, are used as lead replacement additives at some refineries.

Mode of Action

When an unburned fuel/air mixture beyond the boundary of the flame front is subjected to a combination of heat and pressure, detonation may occur. Detonation is characterized by an instantaneous, explosive ignition of at least one pocket of fuel/air mixture outside of the flame front producing an audible sound also called “knock”. At the temperatures found in internal combustion engines, antiknock additives decompose completely into metal, metal oxides and combustible, short-lived hydrocarbon radicals. The metal and metal oxides scavenge radical intermediates, preventing their involvement in combustion reactions. This prevents ignition of unburned fuel during the engine’s expansion stroke, and therefore, knock. Octane quality is defined in terms of resistance to knock, so the capability of an additive to reduce the tendency to knock, by definition, increases the octane quality of the fuel in which it is used. Typical treat rates are in the range 8 - 150 mg/l of active metal.

Anti-Valve Seat Recession

Additives to reduce recession of exhaust valve seats in spark ignition engines employ chemistries which lead to the formation of ash in the combustion process. Known chemistries include phosphorus-based compounds and potassium, sodium and manganese organometallic chemistries.[6,23,24,25]

VSR photo

Purpose

In older engines, certain exhaust valve seat metallurgies, such as soft cast iron, are eroded through the repeated closing and opening contact with the hot exhaust valve. This erosion phenomenon, which had for many years been masked by the use of lead alkyl antiknock additives, became apparent under high speed, high load driving conditions with gasoline containing no added lead. Unchecked, valve seat erosion results in poor valve seal and loss of compression, in turn resulting in power loss, rough engine operation, increased emissions and poor starting. Anti-valve seat recession additives have proved to give effective protection from valve seat erosion in older engines operated on unleaded gasoline.

Mode of Action

Anti-valve seat recession (AVSR) additives function by depositing a thin protective layer on exhaust valve seat surfaces, effectively preventing the metal-to-metal contact which lies at the heart of the erosion process. The protective layer is maintained by combustion of gasoline treated with the AVSR additive, which is usually added at treat levels below 50 mg/kg of the active element. Although some “memory effect” is evident from tests using intermittent treatment with AVSR additives, the best results have been shown to result from consistent use in any engine (with unsuitable metallurgy) operated on unleaded gasoline. Typical treat rates are in the range 100 - 200 mg/kg.

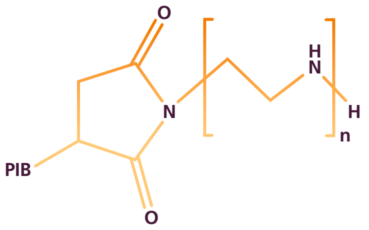
Chemistry of Diesel Fuel Additives

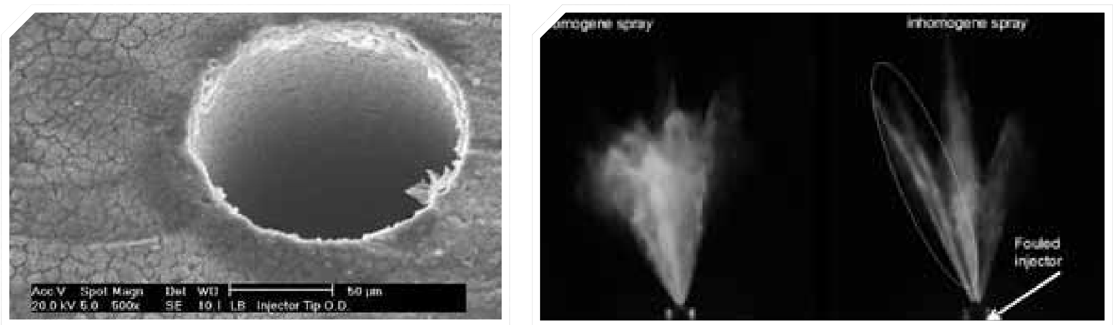
Deposit Control Additives

Deposit control additives (DCAs) for diesel fuel typically employ succinimide chemistry although other proprietary chemistries continue to be introduced into this rapidly developing application. There is a general similarity to DCA used in gasoline, with both products consisting of a polar head which has affinity for metal surfaces in the fuel system and a hydrocarbon tail which allows fuel solubility.

Example of Diesel DCA

PIBSI: Polyisobutylene Succinimide





Injector deposit images / Fuel spray

Purpose

As for gasoline engines, DCAs for compression ignition or "diesel" engines are designed to keep the whole fuel system clean, although in diesel engines intake valves do not come into contact with liquid fuel. In diesel engines the most significant focus for cleanliness lies in the fuel injector which atomises the liquid fuel being delivered into the combustion chamber immediately prior to the onset of combustion during each power stroke.[26,27,28,29,30,31,32,33] Fuel is pumped to extremely high pressures and is forced through very fine orifices during injection. Increasingly strict emissions legislation requires the close control of both the timing of injection and the quantity of fuel injected. Satisfactory engine operation depends very strongly on consistent, long-term control of the drop size distribution and shape of the injected spray inside the combustion chamber. Maintaining injector surfaces in a condition close to the manufactured state is an important factor in maintaining satisfactory long term emissions, power output and fuel economy performance in the diesel engine.

Mode of action

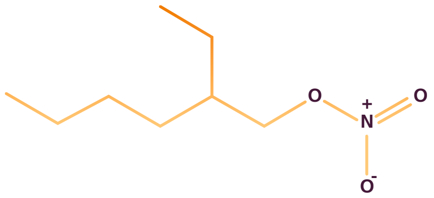
Diesel DCAs help to prevent the formation of deposits in injector nozzles partly by providing a film on metal surfaces and partly by preventing agglomeration of deposit precursors. As for gasoline engines, diesel DCA are normally intended to be used on a continuous basis from a new engine condition to avoid deposit build-up, but by changing the equilibrium of accumulation and removal mechanisms, these additives can also provide a deposit removal function. Typical treatment levels for DCAs, which are frequently combined with other components in multi-functional packages, lie in the range 10 - 200 mg/kg. Treatment levels may be higher to effect removal of existing deposits in engines.

Cetane Number Improvers

Cetane number improver additives are predominantly alkyl nitrates, of which 2-ethyl hexyl nitrate (2-EHN) is the most common, having been used for over eighty years to increase cetane number of diesel fuels. Peroxides such as tertiary butyl peroxide can also be used but are generally less cost effective than alkyl nitrates.

Example of Cetane Number Improver

2-Ethylhexyl Nitrate



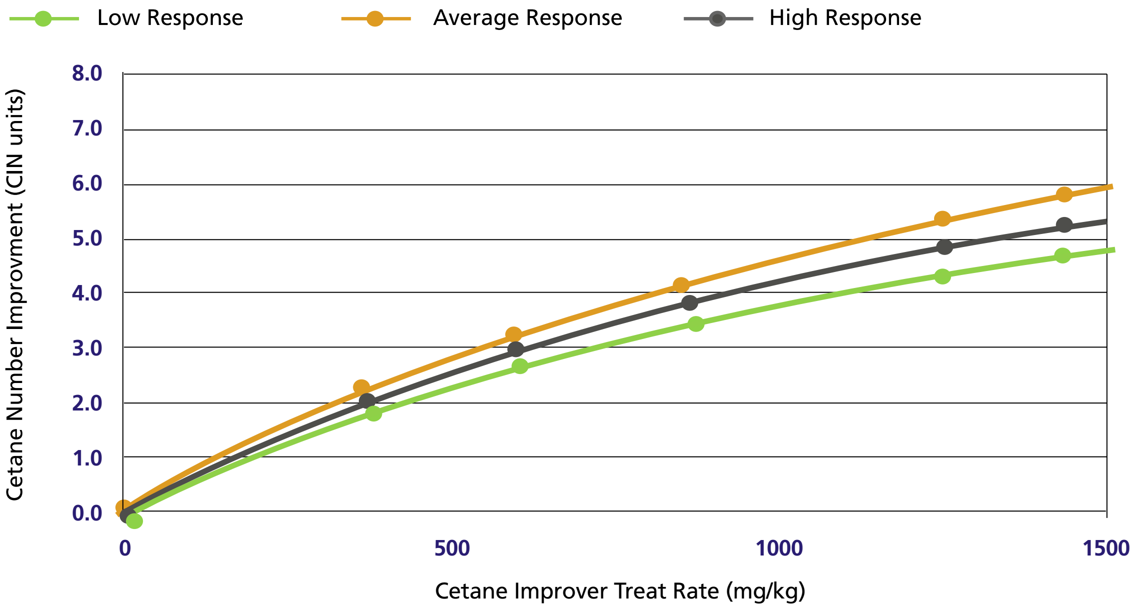


Figure 44 Estimated response to cetane improver of low, medium and high responsiveness diesel

Purpose

Cetane number improvers provide a cost effective increase in diesel cetane quality. Combustion in an engine operating on diesel fuel relies on the auto-ignition of fuel injected into the compressed air trapped in the combustion chamber. After fuel injection, onset of combustion is not immediate but subject to a delay, termed ignition delay. Cetane quality of diesel fuel is defined in terms of the ease with which the fuel ignites; increased cetane number corresponds to reduced ignition delay. Operating a diesel engine on inadequate cetane quality fuel results in poor starting characteristics, especially in cold weather, significant white smoke emissions, higher noise levels, increased fuel consumption and higher exhaust emissions.[34,35,36,37] Higher cetane quality is therefore a very desirable feature in diesel fuels.

Mode of action

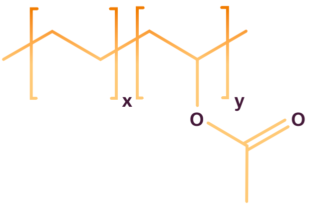
Cetane number improvers break down during combustion to form free radicals. These radicals increase the rate of decomposition of the fuel, causing it to ignite more readily and so reducing ignition delay. Treat levels vary widely from around 0.015 % vol. to 0.2 % vol. and above, with the additive employed at the refinery to trim cetane quality during blending operations to meet product specification but also in multifunctional additive packages where a number of enhanced operational benefits can be demonstrated from increased cetane quality fuel.

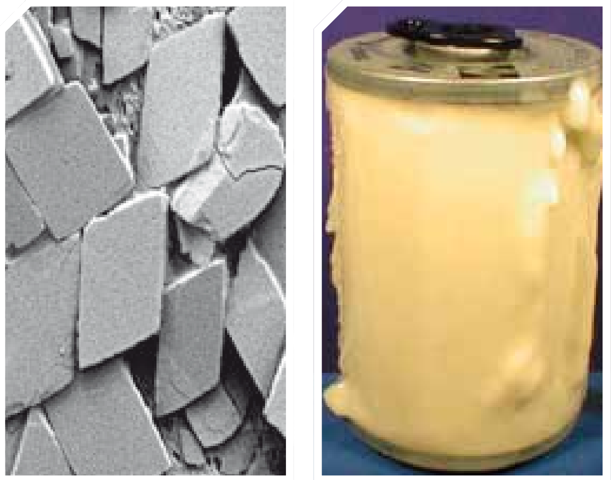
Cold Flow Improvers

Cold flow improver (CFI) additives (also known as Middle Distillate Flow Improvers (MDFI)) for diesel fuels typically utilise vinyl ester co-polymers such as ethylene vinyl acetate (EVA). A range of different low molecular weight polymers with a variety of structures is employed to treat fuels from different crude sources with different hydrocarbon compositions. Other additive chemistries employed include olefin-ester copolymers and dispersants which may be combined with EVA, for example, to prevent wax settlement in fuel storage tanks.

Example of Cold Flow Improver

EVA: Ethylene Vinyl Acetate





Crystal growth / Filter blocking

Purpose

Middle distillate fuels contain typically 20-40% n-paraffins which have several properties desirable in a diesel fuel. In cold weather, however, n-paraffins tend to produce significant volumes of wax crystals. As temperatures drop, crystals grow in size and begin to adhere to each other, forming large lattices of crystals. Uncontrolled, wax crystallisation in diesel fuel can cause vehicle operability problems, blocking fuel filters and feed lines, ultimately leading to power loss and possible engine shutdown.[38,39,40,41,42,43] Use of cold flow improvers in middle distillates prevents these problems and permits a greater proportion of the crude barrel to be included in the diesel pool, resulting in a smaller output of lower value residual fuel and thereby reducing the overall cost of fuel production.

Preventing the formation of large stable lattices does have a negative aspect, in that the crystals do not remain suspended in the diesel fuel, rather they begin to sink towards the bottom of the storage tank. Fuels containing cold flow improver additives, when stored for an extended period in cold weather, can permit fuel quality changes, as fuel in the lower part of the tank becomes wax rich, particularly when the tank fuel level becomes low. Anti-settling additives assist in preventing deposition of wax crystals in treated fuels during tank-storage at refineries and terminals.

Mode of action

Cold flow improver additives function by being only moderately soluble in diesel fuel. As the fuel cools, additive molecules begin to precipitate out of solution as very small nuclei at a temperature close to the cloud point of the fuel. The presence of these nuclei distributed through the fuel encourages the growth of a large number of small wax crystals. Co-precipitation of additive molecules with wax crystals prevents growth of the large plate-like wax crystals seen in untreated fuel. The presence of a large number of small crystals (produced due to the action of a cold flow improver) rather than a small number of large ones, allows the fuel to continue to flow, thus preventing fuel filter and line blockage, and thereby permitting normal engine and vehicle operation at low ambient temperatures. Typical treat levels for CFI additives can range from 50 - 1000 mg/kg.

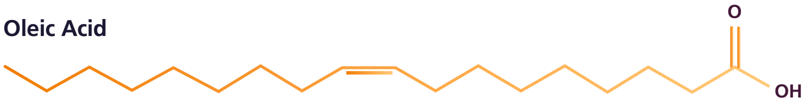
Wax anti-settling additives (WASA), developed to counter wax crystal deposition, function by further reducing the size of wax crystals in the fuel and by dispersing the crystals throughout the body of the fuel. Treat levels for cold flow improver additives vary widely depending on the amount and composition of n-paraffins in the fuel. Optimum treatment of fuel usually results from detailed laboratory analysis followed by performance trials with different additive formulations. A typical treat level for WASA is around 100 - 200 mg/kg.

Lubricity Improvers

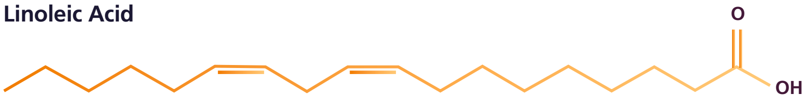
Lubricity additives are surface active compounds, consisting of an active polar head group which permits the formation of a protective film on moving metal surfaces and a hydrocarbon tail to assist fuel solubility. Typical chemistries used in lubricity improvers include fatty acids, esters and amides.

Example of Lubriciy Improver

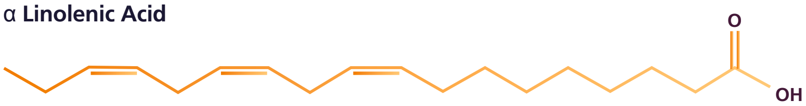
Oleic Acid



Linoleic Acid



α Linolenic Acid



Industry test wear scar

Purpose

Diesel fuel injector pumps frequently rely on the fuel itself to lubricate their moving parts. Modern vehicle emission reduction technology demands almost complete elimination of sulphur from diesel fuels, requiring severe refining processes, primarily hydrotreating, to achieve this. These processes also act to reduce the natural lubricating quality of middle distillate blending components. Untreated, very low sulphur fuels can produce extremely rapid wear, and failure, in both automotive and aircraft fuel pumps. Lubricity improver additives are effective in restoring lubricity lost in severe refinery processing, thereby permitting normal pump operation, reliability and service life.[10,44,45]

Mode of action

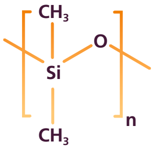
The long chain polar compounds employed in lubricity improver additives permit the establishment of a mono-molecular coating on metal surfaces. This film, or boundary layer, provides a cushion which keeps metal surfaces apart and thus protects against wear. Treat levels, which vary depending on crude source, the level of protection required and the specific additive chemistry employed, lie in the range 25 - 400 mg/kg.

Anti-Foam Additives

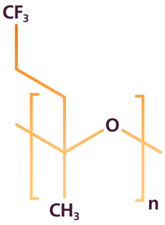
Antifoam additives are polysiloxane based compounds used in multifunctional additive packages.

Example of Anti-Foam

Polydimethylsiloxane



Modified Polydimethylsiloxane



Foam vs. No foam

Purpose

Diesel fuel has a natural tendency to entrain air and form a temporary foam when dispensed from a filling station during vehicle re-fuelling. Foaming is a particular problem for the increasing number of diesel passenger cars, which employ tanks of irregular shapes and narrow filler pipes. With automatic cut-off forecourt dispenser systems, which are now almost universal, foaming leads to premature fuel cut-off and a partially filled tank. Foaming can also result in fuel splashing onto vehicle bodywork or onto the concrete forecourt surface. Neither of these are popular with customers and fuel spilt onto a concrete floor is a safety hazard. Anti-foam additives effectively eliminate these concerns.

Mode of action

Anti-foam additives function by reducing the surface tension of the air bubble walls which constitute the foam, leading to its rapid collapse. Polysiloxane compounds are very effect at low treat levels, typically in the range 2-10 mg/kg.

Corrosion Inhibitors

Corrosion inhibitors for diesel fuel are used for the same purpose, are of the same chemistry and employ the same mode of action as for gasoline. They consist typically of a polar head to enable adhesion to the metal surfaces to be protected, and a hydrocarbon tail to ensure fuel solubility.[5] Effective corrosion inhibitors include carboxylic acids, amines and amine salts of carboxylic acids.

Corrosion inhibitors are applied either at the refinery, pumping station, terminal or as part of a multifunctional additive package.

Example of Corrosion Inhibitor

Dodecenyl Succinic Acid

Purpose

Diesel fuel supply arrangements, like those for gasoline, can permit water to enter fuel, with similar potential for surface corrosion of metallic components throughout the fuel storage and delivery system. Corrosion inhibitor additives are very cost effective in preventing such corrosion.

Mode of action

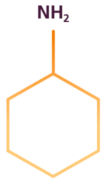
The protective mode of action is the same as in gasoline; the polar head provides a protective film on the metal surface, while the hydrocarbon tail allows the molecule to be solubilised in the fuel. Treat rates are in the range 5-100 mg/kg.

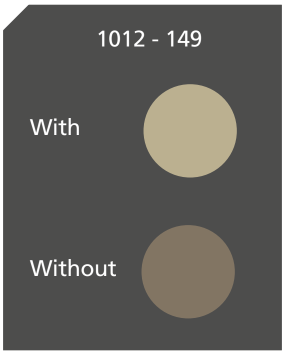
Stability Improvers (incl. Antioxidants)

Diesel stability improver additives are generally long chain and cyclic amines, although antioxidants like those used in gasoline (hindered phenols or aromatic diamines) now also find application in diesel fuel. As with gasoline, instability leads to fuel darkening and the formation of gums and sediments. Stability improvers, like antioxidants, enhance fuel stability and inhibit its tendency to deteriorate in storage.[46,47,48]

Example of Stability Improver

Cyclohexylamine





ASTM D2274 filters

Purpose

Diesel fuel may be stored for prolonged periods, particularly for military use, and it is of prime importance that the fuel remains fit for use throughout this time. Refinery processes to increase the proportion of diesel fuel obtained from a barrel of crude oil have utilised cracked material which contains olefins and more nitrogen and sulphur compounds than straight run distillates. Inclusion of unstable species such as olefins can result in polymerisation to form gums, whilst nitrogen and sulphur compounds and organic acids can combine to form sediments. Due to extensive desulphurisation of fuels at the refinery, reactions involving nitrogen and sulphur species have been significantly reduced, although those same refinery processes have resulted in diesel fuel being potentially susceptible to peroxidation, with consequent gum formation and elastomer embrittlement concerns. As for gasoline, gums are generally undesirable and in diesel fuel systems, sediments can result in fuel filter blockage with implications for vehicle operability.

Mode of action

Stability improvers interfere with the acid-base reactions which occur between nitrogen and sulphur compounds and organic acids, reacting preferentially to produce soluble reaction products and preventing sediment formation. As with gasoline, unstable species in diesel fuel produce free radicals which combine with oxygen to produce further free radicals in a chain reaction and react with olefinic compounds to form gums. Antioxidants inhibit chain-branching reactions or intercept free radicals to form stable hindered radicals which do not propagate further. Typical treat rates are in the range 20 - 200 mg/kg.

Conductivity Improvers

The same Conductivity Improvers are used in diesel fuel as in gasoline.[8] They comprise either fuel-soluble chromium materials, polymeric sulphur and nitrogen compounds, quaternary ammonium salts or complex organic alcohols.

Purpose

Static electricity can accumulate in fuel during pumping operations and this accumulation is exacerbated by physical effects such as pipeline diameter reductions and particularly by in-line filters. Static discharges present an obvious and proven fire hazard particularly for middle distillates such as diesel and jet fuel, especially now that increased refinery processing to remove sulphur has resulted in the production of fuels with extremely low natural conductivities.[48,49] This, together with a trend towards greater switch-loading between gasoline and middle distillates in tankers, has increased the need for higher conductivity fuels, and therefore for anti-static additives, to reduce static accumulation and the risk of fire and explosion during fuel handling.

Mode of Action

Conductivity Improvers greatly enhance the conductivity of the blended fuel, even at very low treat rates. With fuel conductivity above a critical threshold level, static charge accumulation from pumping operations cannot readily occur and charge dissipation rates are increased, thus preventing static discharge. Typical treat rates are in the range 1 - 40 mg/kg.

Metal Deactivators

The metal deactivator (MDA) used in diesel and other middle distillates is N, N'-disalicylidene-1, 2-propanediamine, the same product used in gasoline[4,19].

Purpose

Metal soluble salts present in fuel are known to catalyse oxidation. Copper is particularly associated with fuel instability, even at very low levels. Diesel fuels can be severely destabilised by copper but jet fuel is particularly sensitive to contamination and can fail the Jet Fuel Thermal Oxidation Test (JFTOT) as a result. Addition of MDA generally overcomes this failure and the product is an approved jet fuel additive for this reason.[49,50]

Mode of Action

Metal deactivator additive functions by reacting with dissolved metal in the fuel to form a stable chelate in which the metal has no pro-oxidant effect. Typical treat rates are in the range 4 - 12 mg/kg.

Markers & Dyes

The colouration of diesel fuels employs similar azo and anthraquinone chemistry as already described for use in gasoline.[4]

Purpose

A widespread use of dyes, specific to diesel fuel, is in off-road diesel for use in agricultural and construction machinery (which in many countries carries a reduced fuel duty). A red dye is used in the UK to distinguish between the low duty and higher duty fuels for on-road use and an invisible marker is also included. Markers give no visible effect in the fuel but on extraction with a solvent impart distinctive colours. This technique can be useful in providing inventory control or in deterring theft.

Mode of Action

Markers and dyes are usually added at the refinery or terminal to meet the specific requirement of the client. Treat levels and usage of markers and dyes is also similar to that already described for gasoline.

Dehazers / Demulsifiers / Emulsion Preventatives

Dehazers are complex mixtures of a wide variety of alkoxylate chemistries including phenolic resins, esters, polyamines, sulphonates or alcohols which have been reacted with ethylene or propylene oxide. The products have oil and water soluble tails that allow them to migrate to the fuel / water droplet interfaces where they act.[5,20] They can be applied at refineries, fuel storage systems or designed within finished fuel performance packages to break, or prevent, water based emulsions formed within fuels.

Purpose

Water contamination can be present in fuel anywhere in the distribution system from the refinery storage to the vehicle fuel tank. With agitation, particularly in the presence of other additives, water can become entrained in the form of a stable emulsion within the fuel. Problems associated with emulsions are blockage of fuel filters, promotion of microbial growth and corrosion. Hazy fuel appearance is also evident and this may reduce the value of fuel. Dehazers are emulsion breakers applied to fuels. These additives can be added to hazy fuel in storage to rapidly break otherwise stable emulsions and allow removal of the water from the fuel. Demulsifiers are emulsion breakers applied to lubricating and other oils. Emulsion preventatives are specifically designed to work with other performance package components to prevent the blended fuel and package formulation from forming emulsions with any water contacted within fuel distribution systems.

Mode of action

These products modify the interfacial tension viscosity or film elasticity of water droplets within a fuel emulsion. This allows coalescence and separation of the water droplets from the fuel.

Dehazer and demulsifier dose rates for breaking existing emulsions are typically 10 to 500 mg/kg. Emulsion preventative dose rates are typically 1 to 10 mg/kg.

Fuel Borne Catalysts

Fuel borne catalysts are generally proprietary, fuel soluble organometallic forms of iron, colloidal suspensions of cerium or iron oxide, or a combination. Other chemistries involving copper, manganese, platinum and combinations of metals are also known.

Purpose

Legislative changes in permitted diesel particulate emissions have increasingly required the use of Diesel Particulate Filters (DPFs) which trap emitted carbonaceous particles (soot). Trapping soot is very effective but, if operational difficulties caused by high exhaust back pressure are to be avoided, creates the problem of disposing of the trapped material. The soot is most conveniently, and effectively, removed by combustion within the filter (regeneration). Without some form of catalyst, regeneration requires a high energy input over significant periods of time, which creates a potential fuel consumption penalty estimated to be about 5% of vehicle consumption. Fuel borne catalysts significantly reduce the energy input required to achieve regeneration, and generally facilitate the operation of diesel vehicles fitted with DPFs.[51,52,53,54,55]

Mode of Action

The metallic portion of the fuel borne catalyst added to the diesel fuel survives the combustion process, usually in the form of finely divided oxides. These particles are bound up with agglomerations of tiny soot particles leaving the combustion chamber and pass into the filter. This well distributed catalyst in the soot assists in the process of filter regeneration. A trigger for regeneration of the catalysed soot is typically an energy input in the form of increased exhaust gas temperature, which takes some of the catalysed soot above a threshold ignition temperature. Once combustion is initiated, the accumulated pre-catalysed soot rapidly burns to leave a clean filter and reduced back pressure. Typical active metal treat levels for fuel borne catalysts lie in the range 5-30 mg/kg.

Refinery and Terminal Additives

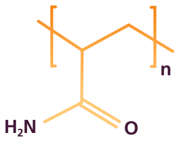
The majority of the fuel additives utilised in refineries and terminals are described in the preceding gasoline and diesel additive sections and will not be reproduced here. There are other additives which have not been described and these are detailed below.

Pipeline Drag Reducing Additives

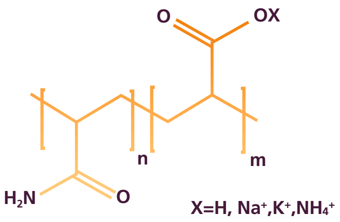
Pipeline drag reducing additives (PDR) are high molecular weight polymers (typically 20-30 million molecular weight) of octene/dodecene/etc. or polyacrylamide suspended in a hydrocarbon solvent.

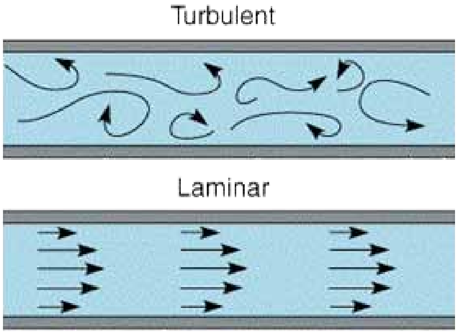
Example of Pipeline Drag Reducing Additive

Polyacrylamide



Partially Hydrated Polyacrylamide





Laminar / turbulent flow

Purpose

When fluids travel through a pipeline, a velocity profile is developed in the flow that varies from zero velocity at the wall of the pipe to a maximum velocity at the centreline of the pipe. This profile is caused by the flow properties in the fluid that create shear layers. At very low velocities, these shear layers are well ordered, and there is no transverse flow between the layers; this is described as laminar flow. As velocities increase, the laminar nature of the flow begins to break down. At the interface between layers, the flow begins to tumble due to shearing, creating transverse flow in which faster moving particles are transported into regions of lower velocity and vice-versa. This turbulent flow causes pressure drops per unit length of pipe and demands higher pumping energy to maintain the bulk velocity of the flow.[56]

The use of PDR products reduces fluid turbulence, especially next to the wall of the pipe, downstream of valves in the pipelines, and at branching points. By decreasing flow turbulence, pipeline drag (pressure loss) is reduced and higher product throughput can be achieved at the same or lower pumping pressures.

Mode of Action

When added to crude oil or refined products in a pipeline, PDR reduce transverse flow, effectively creating a laminar flow. This is especially true close to the pipe walls where flow velocity profile has a very steep gradient in which significant pressure losses occur. Lowering these losses increases the bulk throughput of the pipeline for a given pumping energy, resulting in reduced operating costs.

PDR goes into solution with the fluid in the pipeline and does not coat pipe walls or plate out on valve components. The PDR molecular chain is very fragile and can be sheared or broken by bends in the pipeline, valves, piping branches or when the flow goes through a pumping station. Once the molecular chain is broken, the effectiveness of the PDR is immediately degraded, so it must be re-injected downstream of pumps, valves, and sharp turns in the pipeline to maintain benefits.

Unsheared, PDR can clog filter devices but sheared it passes through filters without problem. PDR are widely used in pipeline systems to facilitate the flow of crude oils, diesel fuels and automotive gasolines. PDR are not permitted in aviation fuels. Typical PDR treat rates are in the range 0.5 - 2 mg/kg for each injection point which results in a total treat rate of 3 - 8 mg/kg.

Anti-Icing Additives

Anti-Icing additives (or Fuel System Icing Inhibitors (FSII)) are used predominantly in military aviation turbine fuel and are typically glycol ethers, such as Ethylene Glycol Mono Methyl Ether (EGME) or Diethylene Glycol Mono Methyl Ether (DIEGME).

Example of Anti-Icing Additive

Ethylene Glycol Methyl Ether

Purpose

During ambient storage and use, aviation turbine fuel (AVTUR) is a clear bright liquid with no evidence of particulate matter or entrained water. During use at altitude however, AVTUR is exposed to extremely low temperatures. AVTUR inevitably contains some water which may have been introduced into the system from the refining process, contaminated fuel storage tanks or condensation in a partially empty fuel tank. Fuel System Icing Inhibitors (Anti-icing additives) reduce the freezing point of any water precipitated from jet fuels due to cooling at high altitudes and prevent the formation of ice crystals which may restrict the flow of fuel to the engine. This type of additive does not affect the freezing point of the fuel itself. Anti-icing additives can also provide some protection against microbiological growth in jet fuel.

Mode of Action

As AVTUR cools at altitude, its ability to retain dissolved water diminishes allowing water molecules to condense and form larger droplets that can freeze in sub-zero temperatures. If such condensation occurs, the water absorbs the FSII from the fuel, which serves to depress the freezing point of the water to < -40 °C. This reduced freezing point prevents the droplet from freezing in fuel tanks, fuel lines or filters and blocking the flow of fuel which could otherwise shutdown an engine. FSII treat rates are required to be in the range 0.1 – 0.2 % by volume, depending upon specification.

Sulphur mitigating additives (H_2S scavengers)

Hydrogen Sulphide (H_2S) “scavengers” are oil or water soluble products that react with H_2S to form low hazard compounds. Product chemistries are varied and include triazine chemistries based on monoethanolamine, methylamine or other amines. They can also be based on nitrogen polymers and non-nitrogen containing aldehydes (formaldehyde is historically an effective scavenger but its use, and reactant waste products, is now environmentally restricted).

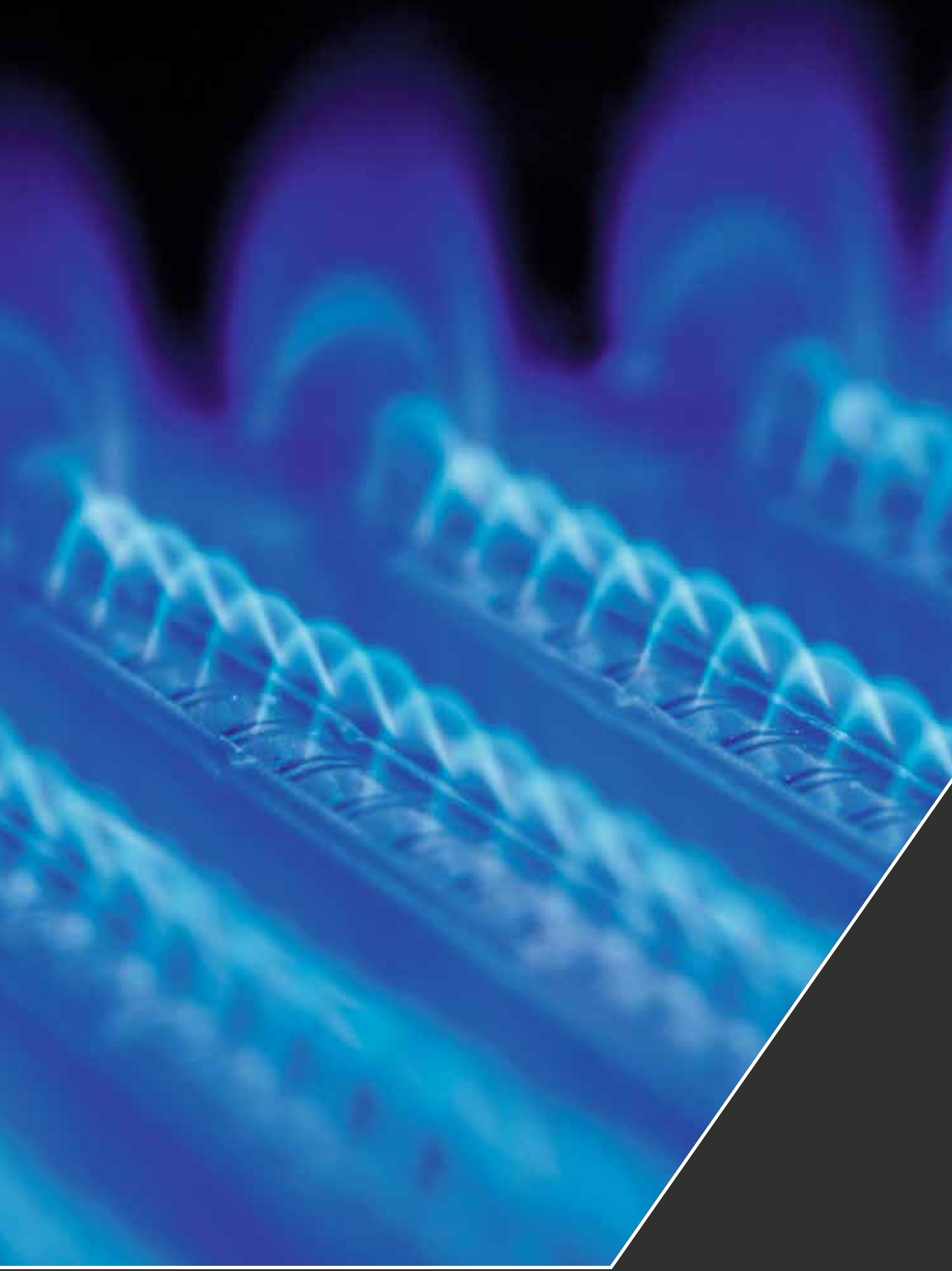
Metallic scavengers are also employed for high temperature applications such as bitumen but their use is limited for other fuel applications.

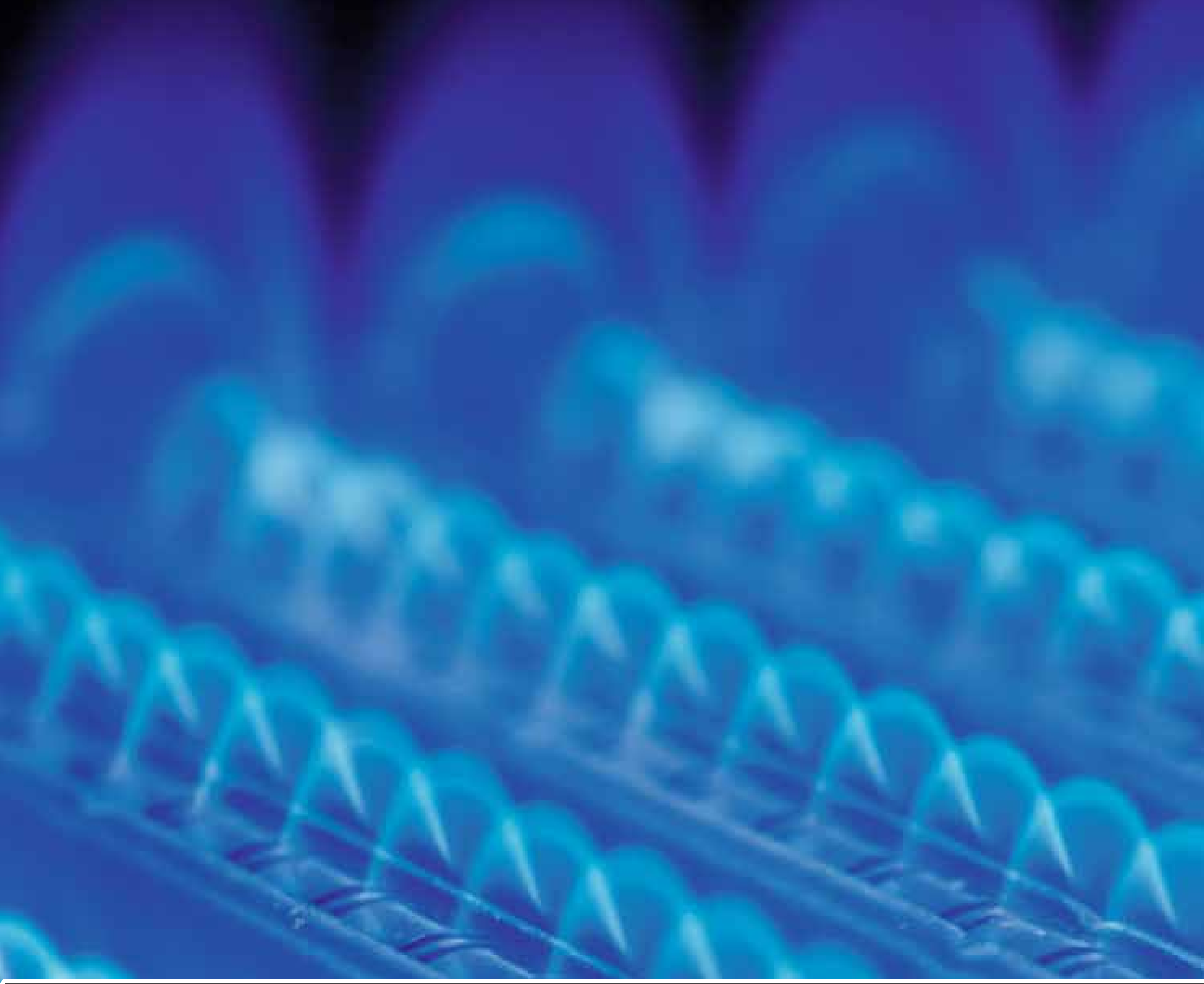
Purpose

H_2S is a toxic gas which can be dissolved or entrained in hydrocarbons by refinery processes or microbial metabolism during fuel degradation. Due to its toxic nature, H_2S is a personnel exposure safety concern but it also accelerates fuel instability and gum formation as well as being a cause of metallic corrosion. H_2S scavengers remove H_2S from hydrocarbon fuels, eliminating these safety and performance concerns.

Mode of Action

The reaction products formed between the scavengers and H_2S are a complex variety of low hazard, stable, sulphur compounds that will not regenerate H_2S. Additives function by chemically reacting with sulphur species to form stable low hazard soluble products. These stable reaction products then degrade in fuel combustion without reverting to Hydrogen Sulphide. A typical treat rate is 5 mg/kg per 50 mg/kg gaseous H_2S released from the hydrocarbon.





Heating Fuel Additives

Heating Fuel Additives

Domestic heating fuel is a middle distillate product typically comprising kerosene meeting BS EN 2869:2010 Class C2. Also in this category of heating fuel is gas oil which is closer in properties to fuel used in compression ignition or diesel engines. Appliances which burn heating fuel comprise central heating boilers with pressure jet burners and stove burners, such as hot pot burners and sleeves burners, with gravity-feed supply systems. In recent years pressure jet burners have been set up to operate on 28 second kerosene fuel, although older systems burning gas oil are still in use. Cooking stoves with pressure-jet burners are becoming more common in response to demands for improved fuel efficiency, greater heat control capability and reduced maintenance costs. Severe maintenance problems with traditional cooking stoves have been experienced since the implementation of the EU reduced sulphur directive in January 2008.

Additives for heating fuels frequently employ similar or related chemistries to those employed in automotive middle distillate fuels, to treat conditions or to resolve issues which may also resemble those encountered in the automotive world.

Stability Improvers (incl. Antioxidants)

Stability improver additives for heating oils are the same as for diesel fuel – please refer to page 27.

Corrosion Inhibitors

Corrosion inhibitors for heating fuel are the same as for diesel fuel – please refer to page 37.

Deposit Control Additives

Deposit control additives for heating fuel are the same as for diesel fuel – please refer to page 32.

Thermal Stability Enhancer

Additives to enhance the thermal stability of heating oil usually comprise dispersants, stabilisers/anti-oxidants and metal deactivator as part of a multifunctional additive package as employed in diesel and other middle distillates. [8,20]


Domestic burner cutaway

Purpose

Instability reactions which occur at elevated temperatures, and which can be accelerated by contact between heating fuel and metallic pipework (if present), are encountered in heating appliances. This can lead to impaired atomisation and combustion and increased soot production from pressure jet burners. Enhanced thermal stability ensures minimal fuel degradation prior to combustion, with optimum performance from the heating appliance.

Mode of Action

Stability improvers interfere with the acid-base reactions which occur between nitrogen and sulphur compounds and organic acids, reacting preferentially to produce soluble reaction products and preventing sediment formation. Unstable species can produce free radicals which combine with oxygen to produce further free radicals in a chain reaction and react with olefinic compounds to form gums. Antioxidants inhibit chain-branching reactions and intercept free radicals to form stable hindered radicals which do not propagate further. Thermal stability additives containing a metal deactivator additionally function by reacting with dissolved metal in the fuel to form a stable chelate in which the metal has no pro-oxidant effect. Typical treat rates vary for the different components but are in the range 50 – 150 mg/kg for dispersants, 10 – 50 mg/kg for stabilisers/anti-oxidants and 4 – 12 mg/kg for metal deactivators.

Lubricity Improvers

Lubricity improvers for heating fuel are the same as for diesel fuel – please refer to page 35.

Combustion Improvers

Combustion improver chemistry employed in heating fuels includes both ashless and metal containing additives. Ashless combustion improver additives typically employ nitrogen functionality on fuel soluble hydrocarbon molecules, while metal containing additives are normally fully fuel soluble organometallic molecules.

Purpose

Incomplete combustion can lead to soot deposits in the combustion chambers, on heat transfer surfaces and in flues of boilers and stoves, which can impair heat transfer and may result in unwanted fires. Combustion improver additives have demonstrated improved efficiency through reduced soot deposition, and have reduced the frequency of flue and chimney fires.

Mode of action

Ashless combustion improver additives function by decomposing early in the combustion process to provide a source of free radicals, which increase the rate of decomposition of the fuel to ensure more complete combustion with reduced formation of sooty particulates. Surface active deposit control chemistry employed for burner nozzle cleanliness can also reduce droplet size during atomisation, with resulting benefits in smoke and soot reduction during combustion. Metal-containing combustion improver additives function by catalysing the burn-out of soot particles formed during combustion, thus reducing the extent and weight of soot deposited on heat transfer and flue surfaces. Typical treat rates are in the range 5 – 50 mg/kg and 150 – 500 mg/kg for metallic and ashless additives respectively.

Cold Flow Improvers

Cold flow improver additives for heating fuel are the same as for diesel fuel – please refer to page 34.

Reodourant Additives

Additives used to reduce the odour of heating oils are typically pinenes derived by turpentine distillation, or may be essential oils and extracts from fruits, nuts, herbs or spices. Choice of aroma is subjective and may result from many trial blends to find the right masking odour.

Purpose

During delivery of heating oil to residential homes, and to a lesser extent during storage, customers may be exposed to the characteristic strongly aromatic odour of the oil which many find objectionable. Reodourant additives counter this odour to give the heating oil a more pleasant, lighter and fresher smell, leading to a greater level of acceptance and fewer customer complaints. Reodourant additives also occasionally find application in automotive diesel.

Mode of action

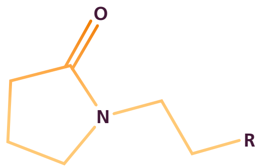
The reodourant additive, when blended with the fuel, masks the natural odour of the heating oil with the chosen fragrance. Selection typically results from a number of customer assessment panel tests, producing the desired overall smell of the reodourant combined with the heating oil. Typical treat rates are in the range 10 – 50 mg/kg.

Marine / Residual Fuel Additives

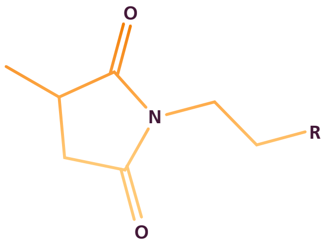
The term Heavy Fuel Oil or Residual Fuel is applied to the refinery product produced from the higher boiling fractions of crude oil which remain after automotive and jet fuels, and lubricant base-stock fractions have been removed. This type of fuel is used where large amounts of energy or power are required from industrial-scale plant, such as refineries, large marine diesel engines, power stations and large-scale industrial heating. Residual fuel properties vary more widely than lighter fuels for automotive or aviation applications, and are more likely to require some type of chemical treatment prior to use. Frequently it is the end-user who decides on the nature and scope of the chemical treatment employed, usually based on an assessment of fuel properties carried out prior to combustion. Although precise additive treatments may vary with the different applications, the fuel characteristics requiring treatment are broadly common to all the uses of heavy fuel oil. To avoid undue repetition, additive treatments will be considered as applying to all the end uses of this fuel.

Examples Of Asphaltene Dispersant

Alkylpyrrolidone

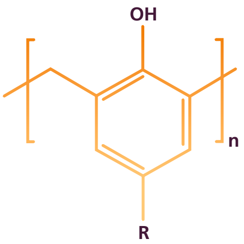


Alkylsuccinimide

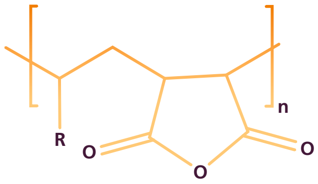


Examples of Ashphaltene Inhibitor

Alkylphenol Formaldehyde Resin (R=C$_{3-24}$ and n=2-12)



Alkene-maleic Anhydride Copolymer



Dispersant / Stabiliser Additives

Dispersant/stabiliser additives typically comprise highly surface active (either anionic of cationic) chemicals used to prevent the precipitation of asphaltenes, which have relatively low solubility in residual fuel oils.[56,57] This type of chemistry frequently has alkaline properties and employs an aromatic carrier solvent.

Purpose

Naturally occurring resins which stabilise electrostatically charged asphaltene micelles in crude oil are lost or altered during refining, thus suppressing the dispersion of asphaltenes. Dilution of heavy fuel oil with paraffinic material (cutter stock) can further increase instability in untreated fuels, resulting in asphaltene agglomeration. This can result in precipitation of sludge in storage and handling equipment, including tanks and filters, and potential operational problems with fuel centrifuges.

Mode of Action

Dispersants/stabilisers have a similar affinity for polar asphaltene molecules as the resins which are altered or lost during refining. Their inclusion maintains fuel stability, keeping asphaltenes in suspension and preventing agglomeration of the micelles into insoluble sludge and deposits. Typical treat rates of dispersant/stabiliser additives lie in the range 50 - 250 mg/kg.

Demulsifiers / Emulsion Preventatives

Emulsion breakers in heavy fuel oils typically comprise traditional chemistries employed for automotive fuels but can also be boosted by asphaltene dispersant type chemistries. They can be applied in fuel storage and handling systems prior to combustion to prevent formation of water-based emulsions within fuels, or to break existing emulsions.[57,58,59]

Purpose

Heavy fuel oils may contain a substantial amount of water, which is not obvious from inspection because of the opacity and dark colour of the fuel. Additive treatment to break up emulsions has been shown to enhance gravitational separation of water from fuel in settling tanks and to reduce the burden on centrifugal separators. An emulsion breaker has also been shown to increase the efficiency of centrifuging, for example to remove catalyst fines, in pre-combustion fuel treatment.

Mode of Action

These products modify the interfacial tension viscosity or film elasticity of water droplets within a fuel emulsion. Droplets of water are encouraged to coalesce, forming a separate layer at the bottom of settling tanks, where the aqueous layer can be removed. Typical treat levels of demulsifier additives lie in the range 50 - 500 mg/kg.

Combustion Improver Additives

Combustion improver additives comprise both ignition improvers, for example to enhance the onset of combustion in large marine compression-ignition engines and also catalysts for the burn-out of carbon produced during combustion. Chemical ashless ignition improvers are organic molecules usually containing reactive nitrogen. Combustion improvers typically contain fuel soluble organometallic compounds based on iron, cerium, magnesium, manganese or other metals.

Purpose

In marine compression ignition engines, improved ignition characteristics assist both with prolonging engine life and reducing maintenance costs. Reduction in the burden of soot produced during combustion, in fuels with a high C:H ratio, decreases carbon deposition in cylinders and on turbocharger blades. More generally, combustion improvers decrease soot deposition rates in fuel economiser heat exchangers and flues. Improved fuel economy, reduced incidence of exhaust fires, lower maintenance costs and less down time are attributed to the use of these additives.[57,58]

Mode of Action

Ignition improvers reduce ignition delay in reciprocating internal combustion engines, thereby reducing both the rate of pressure rise and peak cylinder pressures during combustion. Organic ignition improvers containing nitrogen tested in differential thermal analysis (DTA) showed higher energy outputs and lower peak temperatures in treated samples, probably through the mechanism of increased numbers of active radicals. Organometallic combustion improvers catalyse the onset of carbon combustion, thereby reducing soot deposition during the combustion phase and subsequently in exhaust flues. Typical treat levels of organic ignition improver additives lie in the range 150 - 500 mg/kg, while organometallic combustion improvers are usually treated at a rate of 20 - 200 mg/kg.

Corrosion Inhibitor Additives

Hot corrosion can result from the presence of vanadium, sodium and possibly other metals in combustion ash, while cold corrosion may occur from burning heavy fuel oil of high sulphur content. Hot corrosion additive chemistries comprise soluble organometallic compounds containing magnesium, calcium or silicon.[57,58,59,60] Cold corrosion inhibitor additives are typically organometallic compounds based on magnesium and calcium.

Heat exchanger

Purpose

Ash from combustion of heavy fuel oil frequently contains many inorganic residues. When sodium and vanadium are present above a threshold level and in certain proportions, the ash can form a low melting point slag which will adhere to vulnerable components in reciprocating engines, such as the piston crown, exhaust valves, turbocharger blades etc., resulting in potentially severe corrosion. Inclusion of hot corrosion inhibitor additives in the fuel can limit or prevent this damage. Cold corrosion results typically from acidic condensation products produced by the oxidation of sulphur during the combustion process. Cylinder liners in large compression-ignition engines and exhaust flues in continuous combustion plant are particularly vulnerable.

Mode of Action

Calcium, magnesium and silicon combine with vanadium and sodium metals to produce eutectics with higher melting points than the corrosive slags which could otherwise result when hot corrosion occurs. Melting of the ash is prevented by the use of hot corrosion inhibitor additives, with potentially harmful ash particles being expelled in solid form in the exhaust gases. Magnesium and calcium are also effective in reducing acidity created from combustion of fuel with high sulphur content and are therefore useful in reducing the incidence of cold combustion.[57] Additives containing magnesium, calcium or silicon can be injected into the fuel oil prior to combustion with typical treat levels in the range 100 - 500 mg/kg.

Benefits of Fuel Additives to the Environment And Consumer

Petroleum conservation

Fuel additives have for many decades demonstrated an ability to work synergistically with the internal combustion engine, both optimising the functional efficiency of a given design and also enabling advances in technology to operate efficiently as the moving landscape of engine performance has been realised. Engine specific power outputs have risen significantly over the years, while at the same time engine specific fuel consumption has fallen dramatically. Fuel additives have played an important and active role in these developments which have helped to check or limit automotive fossil fuel consumption.

Biofuels (Including Renewable and Alternative Fuels)

An important factor in the reduction of fossil fuel consumption, and hence containment of carbon dioxide emissions, is the use of renewable or alternative fuels. Ethanol produced from bio-mass, frequently itself the discarded vegetation from food crops, is one such renewable component which can be added to gasoline, with benefits in reduced fossil fuel consumption. Similarly, for compression ignition engines, fatty acid methyl esters (FAME) produced from vegetable oil, often derived from seeds, have been added to diesel fuel for many years to extend crude oil derived fuels. Fuels containing bio-components present special challenges in use, for which a range of additives provide valuable benefits. Aspects include:

Gasoline to which bio-ethanol has been added:

- corrosion of traditional fuel system materials
- possible adverse effect on deposit control performance
- tendency to encounter intake valve sticking problems
- reduced fuel economy

Diesel to which FAME has been added:

- reduced oxidation stability
- potential for increased injector deposit formation
- corrosion in long term storage
- adverse effect on cold flow characteristics
- increased microbial contamination

In both cases, additives play a valuable and very cost effective role in reducing potential operational problems and in meeting fuel specification requirements, which might otherwise prove challenging or impossible without their use.

Fuel economy

Fuel additives benefit fuel economy principally through the mechanism of fuel system cleanliness. Experience has shown that deposits in the air/fuel system in gasoline engines, or in fuel injectors in diesel engines, adversely affect fuel economy. Deposit control additives act to disperse deposit precursors, keeping metal surfaces clean and close to their ‘as-manufactured’ condition. The very high levels of cleanliness now attainable in current high specific output, low specific consumption engines, make a real contribution to maximising fuel economy. The use of friction reducing additives also has a direct effect upon engine operation and can result in additional fuel economy improvements.

Exhaust emissions

Experience has also shown that the same deposits adversely affecting fuel economy will have a deleterious effect on engine exhaust emissions. Increasingly, carbon dioxide is regarded as an exhaust pollutant, emissions of which can be reduced through improved fuel economy. Emissions more traditionally regarded as exhaust pollutants, such as carbon monoxide, unburned hydrocarbons, mixed oxides of nitrogen and, mainly in diesel engines, emissions of particulate matter, may all be adversely affected by deteriorating combustion quality. Unwanted deposits feature strongly as one of the underlying causes of such deterioration in combustion quality and effective additive treatment to prevent deposit formation thus provides a major environmental benefit.

Health, Safety and the Environment

As part of the development process for candidate additive products, chemicals considered for use are carefully screened to minimise any potentially adverse effects on health and safety. An additive is more than just a combination of active ingredients and the selection of the solvents used to bind additive packages together also necessitates close scrutiny to ensure that the total package is acceptable in respect of storage, transportation and use. Aspects considered include the effect on rivers, water courses and the marine environment, plus the potential effect on the atmosphere from products of combustion.

The potential consequences of accidental release of additive products on land, into the atmosphere, in water ways and at sea are important considerations which are included in the development phases of new products. Similarly, potential hazards to personnel during every stage of production, storage and handling are also considered.

Fuel additive user benefits

The range of benefits to the user accruing from fuel additives is very significant and includes:

- Enhanced safety
  - greatly reduced risk of static discharge, which can cause fires and explosions
- Cost saving
  - protection of fuel tanks, pipelines and other equipment from massively expensive corrosion
  - protection of fuel system equipment in diesel and jet engines from catastrophic premature wear
  - reduced pumping costs and energy use in long-distance fuel pipelines
  - reduced refinery processing needed to meet gasoline octane, and diesel cetane, specifications
- Revenue enhancing
  - cold flow improvement in middle distillates, maximising use of high value kerosene for jet fuel
  - stability improvement to prolong storage life of fuels throughout the operating theatre
- Performance enhancement
  - fuel saving from optimised vehicle performance and economy
  - emissions reduction from fuel system cleanliness and combustion optimisation

The Ultimate Fate of Fuel Additives

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 chain and during use. These are, however, limited and not dealt with in this paper.

Fuel additive treat rates are measured in mg/kg and additive consumption is very small relative to the consumption of the fuels themselves. In addition, by far the greatest proportion of any fuel additive consists of carbon, hydrogen and oxygen, with some other elements such as nitrogen.

For the first issue of Document 113, 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 that emissions of both regulated, and unregulated, pollutants linked directly to the combustion of fuel additives (ignoring their emission reduction performance benefits), were insignificant compared to emissions from the base fuel itself.

Fate by element

The greatest proportion of a fuel additive comprises carbon, hydrogen and oxygen. The additive is fully dissolved in the fuel before it enters the engine or burner and is consumed along with the fuel during the combustion process. This process is so complete that, in reality, it is not possible to detect residues from the fuel additive after combustion.

Fate of nitrogen

Some additives contain nitrogen, which might attract the charge of increasing the emissions of mixed oxides of nitrogen (NOx). In practice, however, the amount of nitrogen added is so small compared to the volume which enters the combustion chamber as air (approximately 78 % nitrogen), that the effect is negligible. Testing for increased NOx emissions when the fuel has been treated with additives containing nitrogen has failed to show any measurable difference in NOx emissions.

Other elements

Some additives contain elements other than carbon, hydrogen, oxygen and nitrogen. Two examples are, for older gasoline engines, valve seat recession additives, and for some diesel engines, fuel borne catalysts used to assist regeneration of diesel particulate filters.

Valve seat recession (VSR) additives frequently contain small amounts of either phosphorus, or metals such as potassium, sodium, iron or manganese. The active treat rate of these trace elements usually lies below 50 mg/kg. The great majority of these ash forming elements is deposited on to exhaust valve seats, where a protective layer is formed to provide a form of dry lubrication for exhaust valves. Fate analysis has shown that some of the residue is deposited in crankcase lubricating oil and some in the exhaust system. Undoubtedly a small proportion of the ash residue will be emitted from the tail-pipe in particulate form, however a number of studies have failed to attribute harmful effects to what is, in reality, a very small amount of material from a limited number of older vehicles. The use of such products is expected to reduce over time as other solutions, such as the use of valve seat inserts, become more commonplace and also as the vehicles using VSR additives are, themselves, scrapped.

Use of fuel borne catalyst (FBC) additives in diesel engines has raised some issues over the fate of the metallic component of such additives. These products, however, with active metal treat rates typically in the range 5-30 mg/kg, are employed almost exclusively in combination with a diesel particulate filter (DPF). DPFs which have been developed over the last 25-30 years are extremely efficient and typically eliminate over 99 % of solid particulate matter from the exhaust gases. As a result, the vast majority of metal particles in the exhaust, including those resulting from combustion of lubricating oil or from engine wear processes, are trapped and retained in the filter. Testing has shown that the use of a DPF together with a metallic FBC additive, results in lower overall emissions of metallic particles from the tailpipe than from an untreated fuel without a DPF in the exhaust.

Carbon Dioxide

Since the initial issue of Document 113 more detailed studies on this topic have been undertaken and reported. One commissioned by the German Umweltbundesampt (Environmental Protection Agency) to assemble and evaluate known data concerning relevant mineral oil additives and their products was completed by the Fraunhofer Institute.[61]

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 deposit control additive/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, NOx and particulates formation can be proven. Fuel savings between 2 and 3% appear realistic".

Fuel additives can, and in many cases already do, contribute towards fuel economy and carbon emission reduction either directly or indirectly.[62] Their use enables vehicle performance to be maintained at, or near, optimum over the lifetime of the vehicle. Fuel additives also act as enablers to overcome performance deficiencies of alternative fuels and allow motor manufacturers to design engine components to tighter tolerances as they strive for further emission reduction and fuel economy improvements. Indeed, the importance of additives has already been recognised in European regulation that **"recommends suitable fuel additives without harmful side effects .... to help to avoid deterioration of driveability and emissions control durability"**. It is estimated that 95% of European road fuel is treated with such packages.

Any proposed regulation to mandate the use of fuel additives to assist the reduction of carbon emvissions would, however, require careful consideration and well-developed controls to ensure that effective measures are developed. Fuel additive regulation has the potential to diminish the market forces that currently drive their use at effective levels. Experience from other markets has shown treat rates may reduce to the point of providing less than optimal performance due to the difficulties in implementing a regulatory, as opposed to a market driven, process.

If a regulatory process is to be considered that assesses the contribution of fuel additives to a reduction of carbon emissions, ATC consider it essential that appropriate performance-based measures should be established. These should include essential elements of:

- Standardised test methods based on performance representative of real-world conditions.
- The setting of effective limits based on engine tests developed using sound statistical science with appropriate test fuels.
- An effective process to maintain the integrity, consistency and veracity of the certification test programmes and test laboratories over time.

If the use of fuel additives to assist the reduction of carbon emissions is of interest, ATC would welcome the opportunity to discuss solutions to the above points with relevant industry stakeholders.

As detailed in the section "Benefits of Fuel Additives to the Environment and Consumer", reduction of CO_2 emissions is not the only advantage attributable to the use of fuel additives; additional environmental, as well as safety related and financial benefits, are also associated with the use of these additives.

References

References

1. ATC Document 31 – An Internationally Recognised Nomenclature System for Petroleum Additives
2. Henry J.A., Human & Experimental Toxicology; 1998, 17; 111-123
3. Midgley, T and Boyd T.A., “The Chemical Control of Gaseous Detonation with Particular Reference to The Internal-Combustion Engine”, Ind. Eng. Chem, 14, 894, Oct. 1922
4. Polss P., “What Additives Do For Gasoline”, Hydrocarbon Processing Vol 52 N2 61-68. 1973
5. Owen K., “Gasoline and Diesel Fuel Additives”, Critical Reports on Applied Chemistry, 25, Soc. Chem. Ind., John Wiley & Sons, 1989
6. McArragher J.S., Clarke L. J. and Paesler H., “Prevention of Valve Seat Recession in European Markets”, CEC Fourth International Symposium, Birmingham, May 1993
7. Worldwide Fuel Charter, 4th Edition, November 2006, ACEA, AAM, EMA, JAMA
8. Owen K., and Coley T., “Automotive Fuels Handbook”, Society of Automotive Engineers, 1990
9. Mikkonen S., Karlsson R. and Kivi J., “Intake Valve Sticking in Some Carburettor Engines”, SAE Paper 881643 Oct. 1988
10. Batt R. J., McMillan J. A. and Bradbury I. P., “Lubricity Additives – Performance and No-Harm Effects in Low Sulphur Fuels”, SAE Paper 961943, 1996
11. ATC Document 100, July 2008
12. Kipp K. L., Ingamells J. C., Richardson W. L. and Davis C. E., “Ability of Gasoline Additives to Clean Engines and Reduce Exhaust Emissions”, SAE Paper 700456, May 1970
13. Rentzloff J. B., Plonskert L. and Sneed R. B., “Fuel Detergency - Effects on Emissions”, SAE Paper 720941, Nov. 1972
14. Tupa R. C. and Koehler D. E., “Gasoline Port Fuel Injectors - Keep Clean/Clean up With Additives”, SAE Paper 861536, Oct. 1986
15. Benson J. D. and Yaccarino P. A., “The Effects of Fuel Composition and Additives on Multiport Fuel Injector Deposits”, SAE Paper 861533, Oct. 1986
16. Tupa R. C. and Koehler D. E., “Intake Valve Deposits - Effects of Engines, Fuels and Additives”, SAE Paper 881645, Oct.1988
17. Valtadoros T.H., Wong V. W. and Heywood J.B., “Fuel Additive Effects on Deposit Build-up and Engine Operating Characteristics”, American Chemical Society, Atlanta Meeting, April 1991
18. Dumont R. J., Cunningham L. J. et al, “Controlling Induction System Deposits in Flexible Fuel Vehicles Operating on E85”, SAE Paper 2007-01-4071
19. China P. et al., “Development of a Direct Injection Spark Ignition Engine test for Injector Fouling”, SAE Paper 2003-01-2006
20. Gibbs L. M., “Gasoline Additives - When and Why”, SAE Paper 902104,1990
21. Gilks J.H., “Anti-oxidants for Petroleum Products”, Inst Pet. 50,149, 309-317, 1964
22. Faggan J.E., Bailie J.D., Desmond E.A. and Lenane D. L., “An Evaluation of Manganese as an Anti-knock in Unleaded Gasoline”, SAE Paper 750925, 1975
23. Vincent M.W. and Russell T. J., “A Review of Worldwide Approaches to the Use of Additives to Prevent Exhaust Valve Seat Recession”, 4th Annual Fuels and Lubes Asia Conference, Singapore, Jan. 14-16th 1998

24. Hutcheson R.C., “Valve Seat Recession – An Independent Review of Existing Data”, SAE Paper 2000-01-2015
25. Mulqueen S., Vincent M.W and Mulcare C., “Development of a High Performance Anti-Wear Additive Providing Protection Against Valve Seat Recession Combined With Octane Enhancement in Treated Fuel”, SAE Paper 2000-01-2016
26. Williams D., “Diesel Injector Fouling”, Institution of Mechanical Engineers, Autotech Conference 1989
27. Slack C., Heinze P. and Barry E.G., “Premium Diesel Fuels-Their Role in Diesel Engine Performance”, Proceedings of Institution of Mechanical Engineers Seminar on Diesel Fuel Injection, London, Oct. 1989
28. Reading K., Roberts D.D. and Evans T.M., “The Effects of Fuel Detergents on Nozzle Fouling & Emissions in IDI Diesel Engines”, SAE Paper 912328, 1991
29. Leedham A., Caprotti R., Graupner O. and Klauna T., “Impact of Fuel Additives on Diesel Injector Deposits”, SAE paper 2004-01-2935
30. Breakspear A., Caprotti R., Graupner O. and Klauna T.,, “Detergency Requirements of Future Diesel Injection Systems”, SAE paper 2005-01-3901
31. Barbour R. et al, “Diesel Detergent Additive Responses in Modern, High-Speed, Direct-Injection, Light-Duty Engines”, SAE Paper 2007-01-2001
32. Birgel A. et al, “Deposit Formation in the Holes of Diesel Injector Nozzles: A Critical Review”, SAE Paper 2008-01-2383
33. Schwab S.D. et al, “Internal Injector Deposits in High-Pressure Common Rail Diesel Engines”, SAE Paper 2010-01-2242
34. Aradi A.A and Ryan T.W, “Cetane Effect on Diesel Ignition Delay Times in a Constant Volume Combustion Apparatus” SAE Paper 952352, 1995
35. Green G.J., Henley T.J., Starr M.E., Assanis D.N., Syrimis M. and Kanafani F., “Fuel Economy and Power Benefits of Cetane Improved Fuels in Heavy Duty Diesel Engines” SAE Paper 972900, 1997
36. Becker R.F., Ndiomu P. and Hoskin D.H., “Reduction in Particulate and Black Smoke in Diesel Exhaust Emissions” SAE Paper 972903, 1997
37. Barbier P., “Evaluation of Cetane Improver Effects on Regulated Emissions from a Passenger Car Equipped with a Common Rail Diesel Engine”, SAE Paper 2000-01-1853
38. Holder G. A. and Winkler J., “Wax Crystallisation From Distillate Fuels”, J Inst Pet. Vol 51 No 499, 1965
39. “The Cold Filter Plugging Point of Distillate Fuels”, Report No. CEC P-01-74, 1974
40. Coley T., “Low Temperature Operability of Diesels”, SAE Paper 830596, 1983
41. Taylor M. G. and Rossi F., “New Flow Improver Technology for Increased Refinery Economics of Distillate Production”, AFTP presentation, Paris, Nov. 1983
42. Brown G. I., Tack R. D. and Chandler J. E., “An Additive Solution to the Problem of Wax Settling in Diesel Fuels”, SAE Paper 881652, 1988
43. Chandler J. E., Horneck F. G. and Brown G.I., “The Effect of Cold Flow Additives on Low Temperature Operability of Diesel Fuels”, SAE Paper 929186, 1992
44. Hitchens G. J., Pearson M. and Robertson S.D., “Lubricity Additives for Low Sulphur Diesel Fuels”, 5th CEC Symposium, Gothenburg, May 1997
45. Lin J. and Caprotti R., “Lubricity Additives - Chemistries and Potential Harms”, Motor Fuels 2002, Slovak Republic
46. Pedley J.F., Hiley R.W. and Hancock R.A., “Storage Stability of Petroleum-Derived Diesel Fuel”, Fuel Vol. 66, pp 1646-1651, Dec. 1987
47. Mabley P.B., Morris J. D. and Wallace G.M., “Distillate Fuel Stability in a Major European Refinery”, 3rd International Stability & Handling of Liquid Fuels Conference, London, Sep. 1988
48. Schwab S.D., Henley T.J., Moxley J.F. and Miller K.T., “Thermal Stability of Diesel Fuel”, 7th International Conference on Stability and Handling of Liquid Fuels, Sep. 2000

References

49. Turbine Fuel, Aviation Kerosine Type, Jet A-1. Ministry of Defence (UK) Standard 91-91, Issue 6, 2008-08-25.
50. Standard Specification for Aviation Turbine Fuels, ASTM D1655-09a (2010). ASTM International, West Conshohocken, Pennsylvania, USA
51. Pattas K., Samaras D., Sherwood K., Umehara J. and Lemaire J., “Cordierite Filter Durability With Cerium Fuel Additive: 100,000 km Revenue Service in Athens”, SAE paper 920363, 1992
52. Lepperhoff G., Lüders H., Barthe P. and Lemaire J., “Quasi-Continuous Particle Trap Regeneration by Cerium Additives, SAE paper 950369, 1995
53. Richards P., Terry B., Vincent M.W. and Cook S.L., “Assessment of the Performance of Diesel Particulate Filter Systems With Fuel Additives for Enhanced Regeneration Characteristics”, SAE Paper 1999-01-0112 (1999)
54. Vincent M.W. and Richards P.J., “The Long Distance Road Trial of a Combined Diesel Particulate Filter and a Fuel Additive”, SAE Paper 2000-01-2849 (2000)
55. Guinther G H., Human D.M., Miller K.T., Roos J.W. and Schwab S.D., “The Role That Methylcyclopentadienyl Manganese Tricarbonyl (MMT) can Play in Improving Low Temperature Performance of Diesel Particulate Traps”, SAE Paper 2002-01-2728 (2002)
56. Investigation of Pipeline Drag Reducers in Aviation Turbine Fuels, CRC Report No. 642, October 2005
57. in Aviation Turbine FuelsLeigh-Jones C. “A Practical Guide to Marine Fuel Oil Handling” Institute of Marine Engineering, Science and Technology, MEP Series Vol 3 Part 19 section 12 p 103, 1998
58. CIMAC (Conseil International des Machines à Combustion) Guide No 25, section 7 pp 42-45, 2006
59. Class NK (Japanese Classification Society), “Guidance for Measures to Cope With Degraded Marine Heavy Fuels Version II”, pp 116-117, 2008
60. American Bureau of Shipping, “Notes on Heavy Fuel Oil”,section 3 pp 22-26, section 7 pp 54-55, 2001
61. Keller, D., Boehncke, A. and Mangelsdorf, I., Fraunhofer Institute for Toxicology and Aerosol Research, Hanover, June 1999; Research Report UBA FuE – Plan 204 02 836; Assembly and Evaluation of the Known Data concerning Relevant Mineral Oil Additives and their Combustion Products
62. Reduction of CO2, ATC Document 96, November 2008

Appendix

TEST METHODS AND PERFORMANCE ASSESSMENT

Testing and Standardisation Organisations

Two Testing and Standards bodies are referred to in this Appendix, ASTM and CEC.

ASTM International, formerly known as the American Society for Testing and Materials (ASTM), is a globally recognized leader in the development and delivery of international voluntary consensus standards. Today, some 12,000 ASTM standards are used around the world to improve product quality, enhance safety, facilitate market access and trade, and build consumer confidence.

CEC is an Industry-based organisation which develops test methods for the performance testing of automotive engine oil, fuels & transmission fluids (using gasoline & diesel engines). In addition, it covers marine & large engine oils, two-stroke engine oils & associated bench tests

Engine Test Procedures

Various engine test methods are available to measure the efficiency of Deposit Control Additives. Performance in different parts of the engine must be assessed by the appropriate test method as there is no single test that covers all aspects. Engine tests are run according to complex and costly procedures, often requiring long durations (3 to 7 days) and significant amounts of fuel (up to 1000 litres).

Gasoline Injector cleanliness test methods

ASTM D5598 - 01(2007) Standard Test Method for Evaluating Unleaded Automotive Spark-Ignition Engine Fuel for Electronic Port Fuel Injector Fouling

Summary

Driveability problems in PFI automobiles were first reported in 1984. Deposits are prone to form on the metering surfaces of pintle-type electronic fuel injectors. These deposits reduce fuel flow through the metering orifices. Reductions in metered fuel flow result in an upset in the air-fuel ratio, which can affect emissions and driveability. When heavy enough, these deposits can lead to driveability symptoms, such as hesitation, hard starting, or loss of power, or a combination thereof, that are easily noticed by the average driver and that lead to customer complaints. The mechanism of the formation of deposits is not completely understood. It is believed to be influenced by many factors, including driving cycle, engine and injector design, and composition of the fuel. The procedure in this test method has been found to build deposits in PFIs on a consistent basis. This procedure can be used to evaluate differences in base fuels and fuel additives.

ASTM D5598 uses a vehicle equipped with a 2.2L Daimler turbocharged four cylinder engine to run a test procedure to evaluate the tendency of an unleaded spark-ignition engine fuel to foul electronic port fuel injectors (PFI).

Gasoline Intake valve cleanliness test methods (IVD)

CEC F-05-93 - Inlet Valve Cleanliness in the MB M102E Engine

Summary

This test method is designed to evaluate the propensity of gasoline or gasoline additive formulations to prevent intake valve deposits in fuel injected engines.

The engine is operated for a period of 60 hours under cyclic conditions, simulating stop and go operation, with the inlet valve pegged to prevent rotation. The ability of a gasoline or a gasoline formulation to influence deposit formation on the inlet valves is determined. The results are expressed by the weight of the deposits accumulated during the test on the intake valves and in terms of merit rating.

The test utilizes a Mercedes Benz M102E in-line, 4-cylinder, 4-stroke, 2.3L gasoline engine mounted on a computer controlled test-bed having 1 Hz data logging capability and usual services such as exhaust extraction, fuel flow measurement, temp and pressure measurements etc.

CEC F-20-98 - Deposit Forming Tendency on Intake Valves

Summary

This test method is designed to evaluate the propensity of gasoline or gasoline additive formulations to prevent intake valve deposits in fuel injected engines. The test time is 60h under cyclic conditions. Results of tests run are presented as a weight of the inlet valve deposits. This test method no longer supports the evaluation of combustion chamber deposit measurement, however, a method for collecting such deposits is described. There is no precision data available for CCD measurement.

The test utilizes a Mercedes Benz M111, 2.0 litre, 16 valve, naturally aspirated, lambda controlled, electronic fuel injected gasoline engine. Cylinder heads are re-built with new, pegged inlet valves. Engines are used for multiple tests.

ASTM D5500 - 98(2008) - Standard Test Method for Vehicle Evaluation of Unleaded Automotive Spark-Ignition Engine Fuel for Intake Valve Deposit Formation

Summary

It was determined through field testing that intake valve deposits could adversely affect the driveability of certain automobiles. Testing concluded that if an gasoline could keep intake valve deposits at, or below, a certain average weight per valve at the end of mileage accumulation, then that fuel could be used in the BMW vehicle-engine combination for a specified period without intake valve deposits causing driveability degradation. Minimizing intake valve deposits was identified as necessary to maintaining vehicle driveability and tailpipe emissions control.

This test method uses a 1985 model BMW 318i vehicle. Mileage is accumulated following a specified driving schedule on either public road or test track. Chassis dynamometers shall not be used for this test procedure as no correlation between road operation and chassis dynamometers has been established.

ASTM D6201 - 04(2009) Standard Test Method for Dynamometer Evaluation of Unleaded Spark-Ignition Engine Fuel for Intake Valve Deposit Formation

Appendix

Summary

The Coordinating Research Council (CRC) sponsored testing to develop this test method to evaluate a fuel's tendency to form intake valve deposits.

This test method covers an engine dynamometer test procedure for evaluation of intake valve deposit formation of gasoline. This test method uses a Ford Ranger 2.3 L four-cylinder engine.

Gasoline no-harm test methods

CEC F-16-96 - Assessment of the Inlet Valve Sticking Tendency of Gasoline Fuels

Summary

The test method is designed to determine whether gasoline is likely to cause inlet valve sticking. When an engine has stood for several hours, a small quantity of fuel may collect in the annulus between the valve stem and guide. If the fuel / fuel additive combination should be prone to increased viscosity and sticking tendency at low temperatures, then this could affect the operation of the inlet valves, and in severe cases the valve could stick in the open position which will prevent the engine from starting.

The test utilises a 1.9L water-cooled, opposed 4-cylinder VW Waterboxer Gasoline Engine; this flat engine design is known to be susceptible to valve sticking. Test results are either a Pass (where no sticking of the intake valve is detected as measured in accordance with the test method) or a Fail (where intake valve sticking is detected). As such normal CEC statistical targets do not apply in this test.
Combustion chamber deposit test methods (CCD)

These are used to assess any possible contribution to accumulation of deposit from partially combusted fuel, oil and additives components in the combustion chamber. Usually Combustion Chamber Deposits are measured as part of an IVD test such as CEC F20-A-98 and ASTM D6201 mentioned above.

Diesel Injector cleanliness test methods

CEC F-23-01 - Procedure for Diesel Engine Injector Nozzle Coking Test

Summary

The test is designed to evaluate the injector nozzle coking propensity of diesel fuels.

The test uses a PSA XUD9 (A/L), 1.9 litre, 4 cylinder, indirect injection diesel engine. The engine is operated at light load/speed and with cyclic conditions for a period of 10 hours using injectors with "unflatted" needles. The propensity of the fuel to cause deposit formation in the injectors is determined by measuring the injector nozzle air flow before and after the test operation. The results are expressed in terms of the percentage airflow reduction at needle lift values of 0.1, 0.2 and 0.3 mm needle-lift for all 4 nozzles. The performance criterion is a single value of the average percentage air-flow reduction at 0.1 mm lift of all 4 nozzles.

CEC F-98-08 - Direct Injection, Common Rail Diesel Engine Nozzle Coking Test

Summary

The indirect injection engine has now given way in the market to more modern, direct injection, light duty diesel engines, for reasons of fuel economy, performance and low emissions. These engines are much more sophisticated than indirect injection types, and must retain all their calibration precision in order to maintain their design performance. The injectors are vulnerable to having their operation impaired by fouling from the deposits resulting from combustion and, for this reason, the DW10 Nozzle Fouling test was developed to demonstrate the potential of fuels to cause fuel injector fouling in these modern engines and also to demonstrate the ability of detergent fuel additives to prevent or control these deposits.

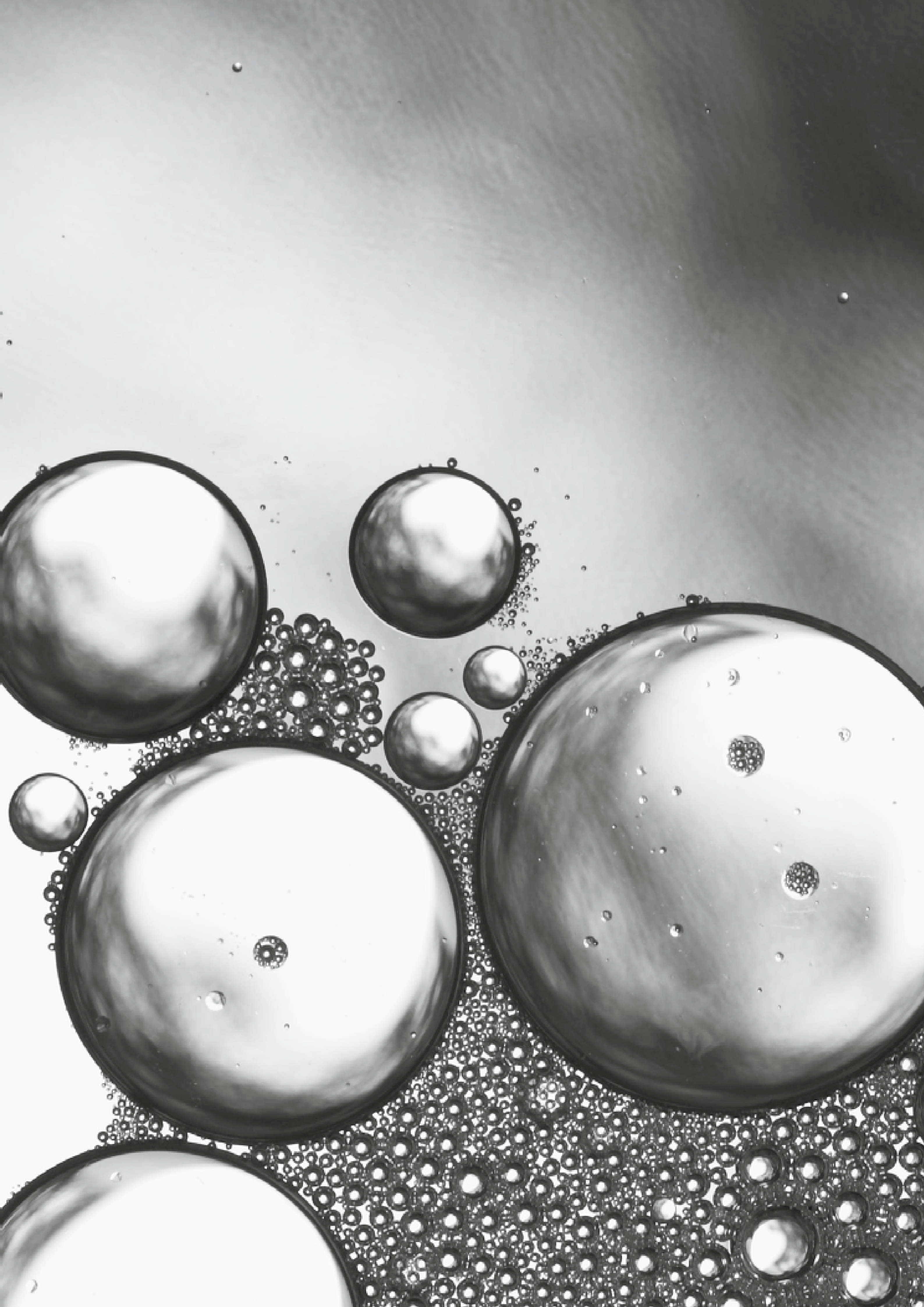
The test uses a Euro 4 PSA DW10 2.0L, common-rail, 4 cylinder, turbo-charged engine fitted with Euro 5 injectors mounted on a test-bed The test cycle consists of 12-stages and lasts 1hour. New injectors are bedded-in for 16 cycles on the non-fouling DF79 fuel, test fuel is then flushed through the engine and the test is runs for 8 cycles before stopping for 4 hours. This is repeated 3 times and test finishes after a further 8 cycles. The percentage power loss at Stage 12 over the 32 cycles is the final result of this test.

The objective of the test is to discriminate between fuels that differ in their ability to produce injector deposits. The target is to be able to discriminate between a fuel that produces no measurable deposits and one which produces deposits that cause the 2% loss in power considered unacceptable by engine manufacturers.

Laboratory Test Procedures

Various laboratory test procedures are employed to demonstrate the performance of fuel additives. These include:

- ASTM D665 - 06 Standard Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water
- ASTM D2274 - 10 Standard Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method)
- ASTM D6079 - 11 Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR)
- ASTM D6371 - 05(2010) Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels
- ASTM D97 - 11 Standard Test Method for Pour Point of Petroleum Products
- ASTM D525 - 05 Standard Test Method for Oxidation Stability of Gasoline (Induction Period Method)
- ASTM D2624 - 09 Standard Test Methods for Electrical Conductivity of Aviation and Distillate Fuels
- ASTM D2699 - 11 Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel
- ASTM D2700 - 11 Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel
- ASTM D613 - 10a Standard Test Method for Cetane Number of Diesel Fuel Oil
- ASTM D7668 - 10 Standard Test Method for Determination of Derived Cetane Number (DCN) of Diesel Fuel Oils - Ignition Delay and Combustion Delay Using a Constant Volume Combustion Chamber Method



SEPTEMBER 2013 / ATC DOCUMENT 113

ATC

A SECTOR GROUP OF cefic

Technical Committee of Petroleum Additive Manufacturers in Europe