ATC

Fuel Additves : Use & Benefits

Revised and enlarged edition of ATC technical brochure

Agenda

Presentation of ATC industry body

- Purpose of ATC
- Organisation
- Membership

Presentation of the Fuel Additives Group (FAG)

- Membership
- Typical achievements & activities

Introduction of **Document 113** “Fuel Additives : Use and Benefits”

- Origin of Document 113
- Definition of fuel additive, industries & markets covered
- Market size (EU27)
- Description of fuel additives use and benefits in various fields

Agenda

Presentation of ATC industry body

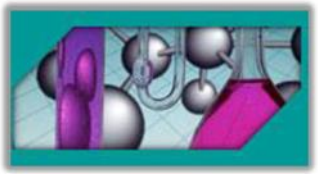
- Purpose of ATC
- Organisation
- Membership

Presentation of ATC Industry Body

The Technical Committee of Petroleum Additives Manufacturers in Europe (ATC) was established in 1974 and became affiliated as an industry sector group of CEFIC in 1979.

Purpose of ATC :

To provide a forum for all Petroleum Additive Companies within Europe to **discuss developments of a Technical or Regulatory nature**



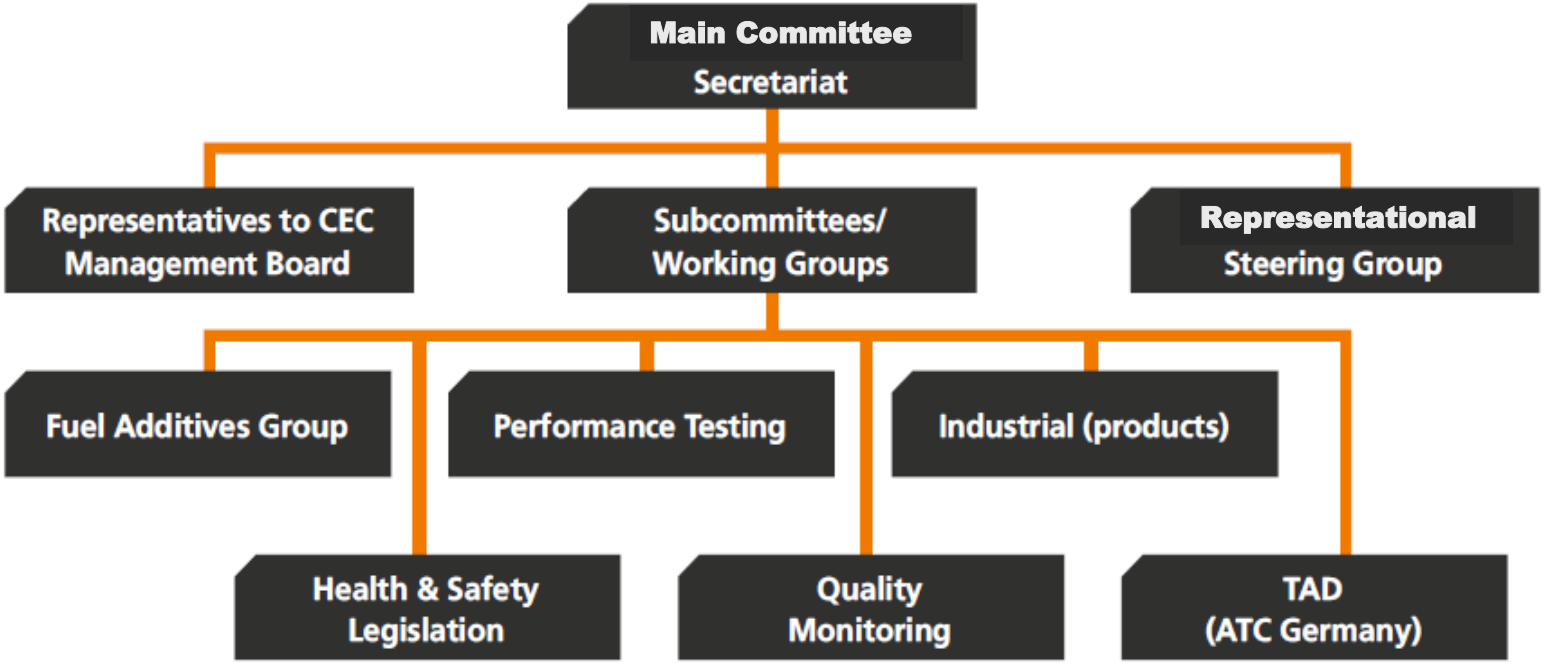
To develop, agree and **publish industry positions** where appropriate

To ensure **communication with other industry** stakeholder groups

To participate **actively in industry test development and maintenance work** to assure **quality and fairness** in product performance testing

Presentation of ATC Industry Body

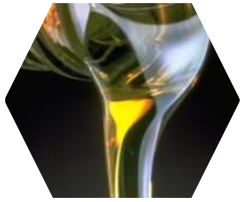
ATC organization :



CEC : Coordination European Council for the Development of Performance Tests for Lubricants and Engine Fuels

Presentation of ATC Industry Body

Fully engaged with associated industry technical bodies :



Presentation of ATC Industry Body

ATC membership : open to all companies which operate chemical processes for the manufacture of petroleum additives, or have comprehensive test facilities, in Europe. Additives companies fulfilling these requirements outside Europe are eligible to apply for associate membership if they are active in the distribution or sale of petroleum additives in the Region

innospec fuel specialties

Nouryon

TOTAL

TOTAL ACS

CRODA

EVONIK INDUSTRIES

LANXESS

Afton CHEMICAL

BASF We create chemistry

Infineum

Associate members:

DORF KETAL

Lubrizol

VeryOne Fuel Improvers

SONGWON

Chevron Oronite

ATC

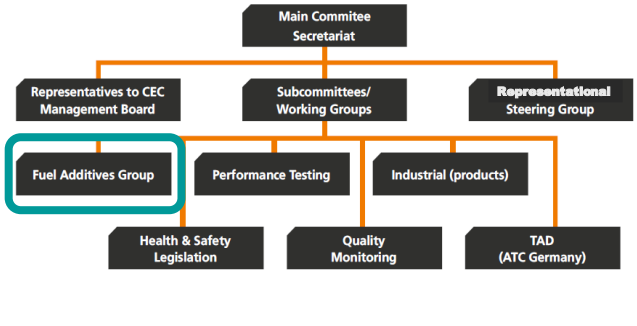
Agenda

Presentation of the Fuel Additives Group (FAG)

- Membership
- Typical achievements & activities

The Fuel Additive Group (ATC)

The working group of ATC dedicated to **Fuel Additives** :



Membership :

Afton CHEMICAL

Nouryon

BASF We create chemistry

Infineum

VeryOne Fuel Improvers

TOTAL ACS TOTAL

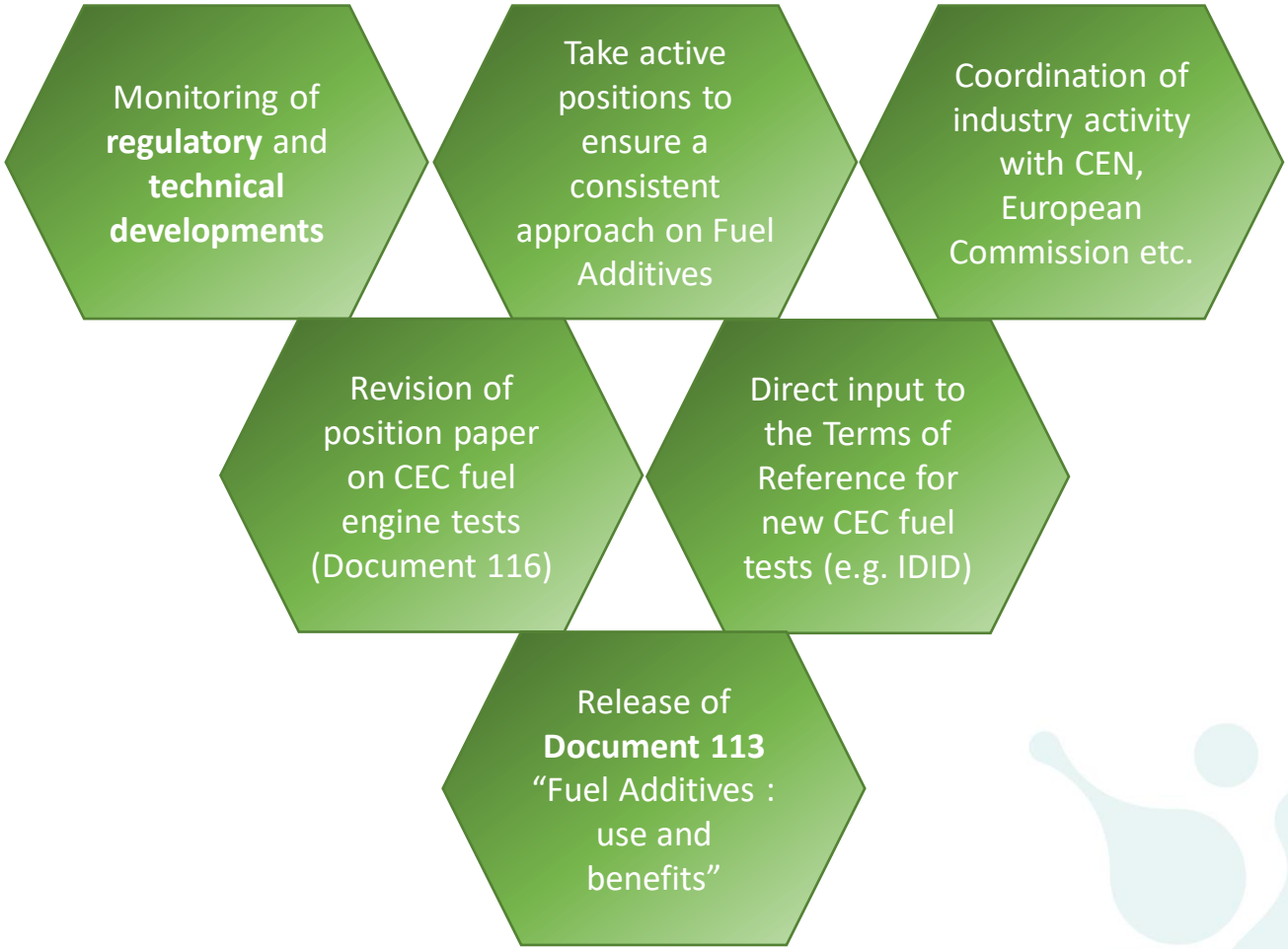
Lubrizol

innospec fuel specialties

Associate member : DORF KETAL

The Fuel Additive Group (ATC)

FAG typical activities and recent achievements :



Agenda

Introduction of **Document 113**

“Fuel Additives : Use and Benefits”

- Origin of Document 113
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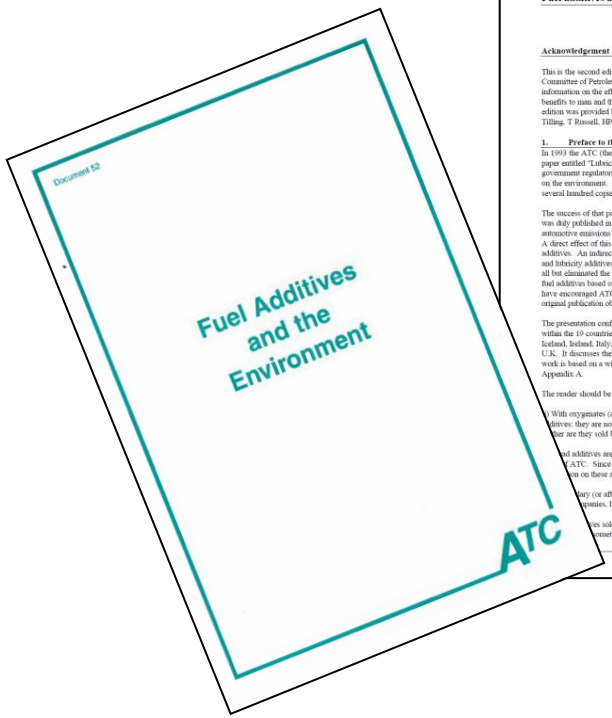
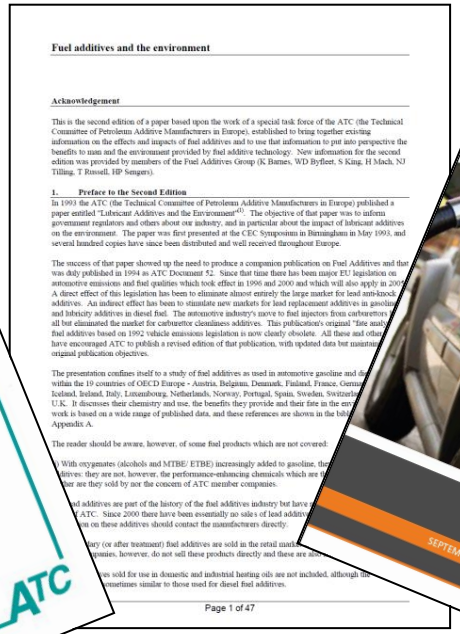
Fuel Additives : Use & Benefits

Document 113 issued in 2013 by a specific FAG task force :

Document 52
First published 1994

Updated
2005




Fuel additives and the environment

Acknowledgement

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

1. Preface to the Second Edition

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

The success of that paper showed up the need to produce a companion publication on Fuel Additives and that was duly published in 1994 as ATC Document 52. Since that time there has been major EU legislation on automotive emissions and fuel qualities which took effect in 1996 and 2000 and which will also apply in 200
A direct effect of this legislation has been to eliminate almost entirely the large market for lead anti-knock additives. An indirect effect has been to stimulate new markets for lead replacement additives in gasoline and lubricity additives in diesel fuel. The automotive industry's move to fuel injectors from carburettors all but eliminated the market for carburettor cleanliness additives. This publication's original "fire analy fuel additives based on 1992 vehicle emissions legislation is now clearly obsolete. All these and other have encouraged ATC to publish a revised edition of that publication, with updated data but maintain original publication objectives.

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

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

) With oxygenates (alcohols and MTBE/ ETBE) increasingly added to gasoline, the ditives: they are not, however, the performance-enhancing chemicals which are th ther are they sold by nor the concern of ATC member companies.

ad additives are part of the history of the fuel additives industry but have y of ATC. Since 2000 there have been essentially no sales of lead additi ion on these additives should contact the manufacturers directly.

ary (or after treatment) fuel additives are sold in the retail mark mpanies, however, do not sell these products directly and these are also

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

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Document 113
2013

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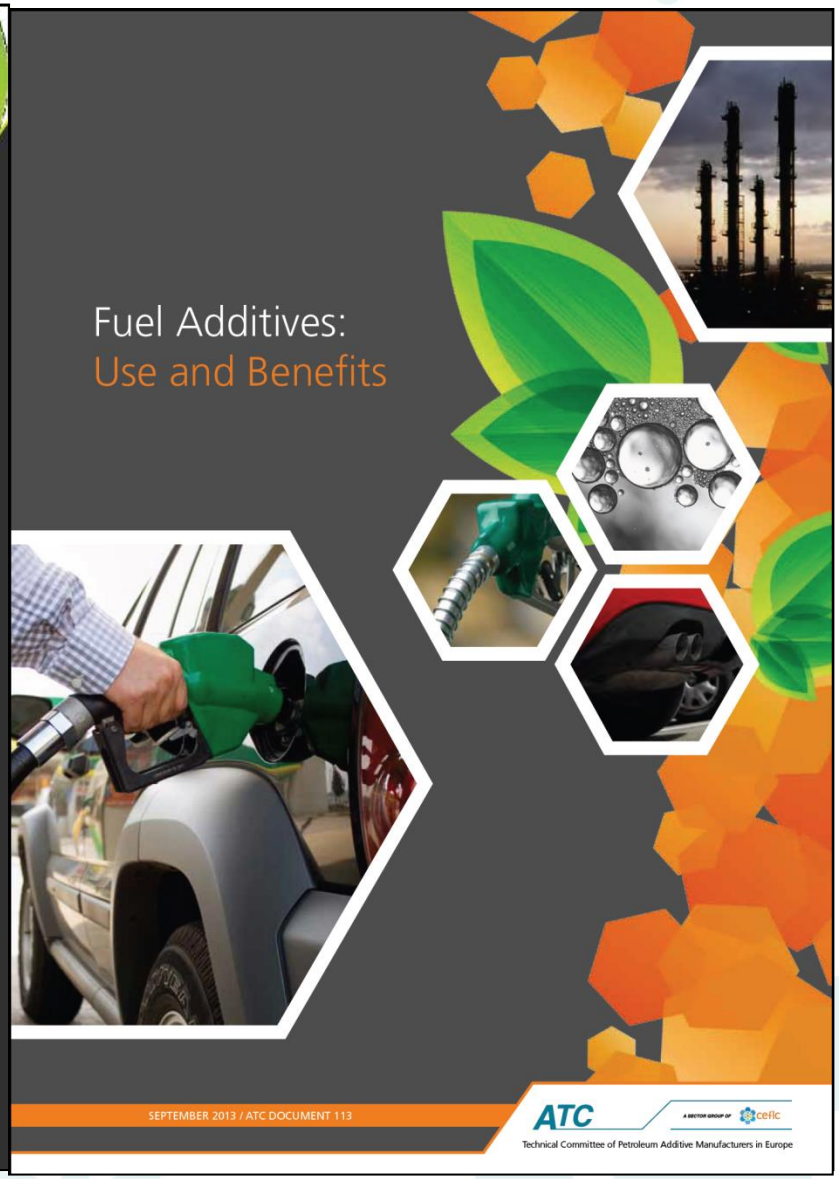

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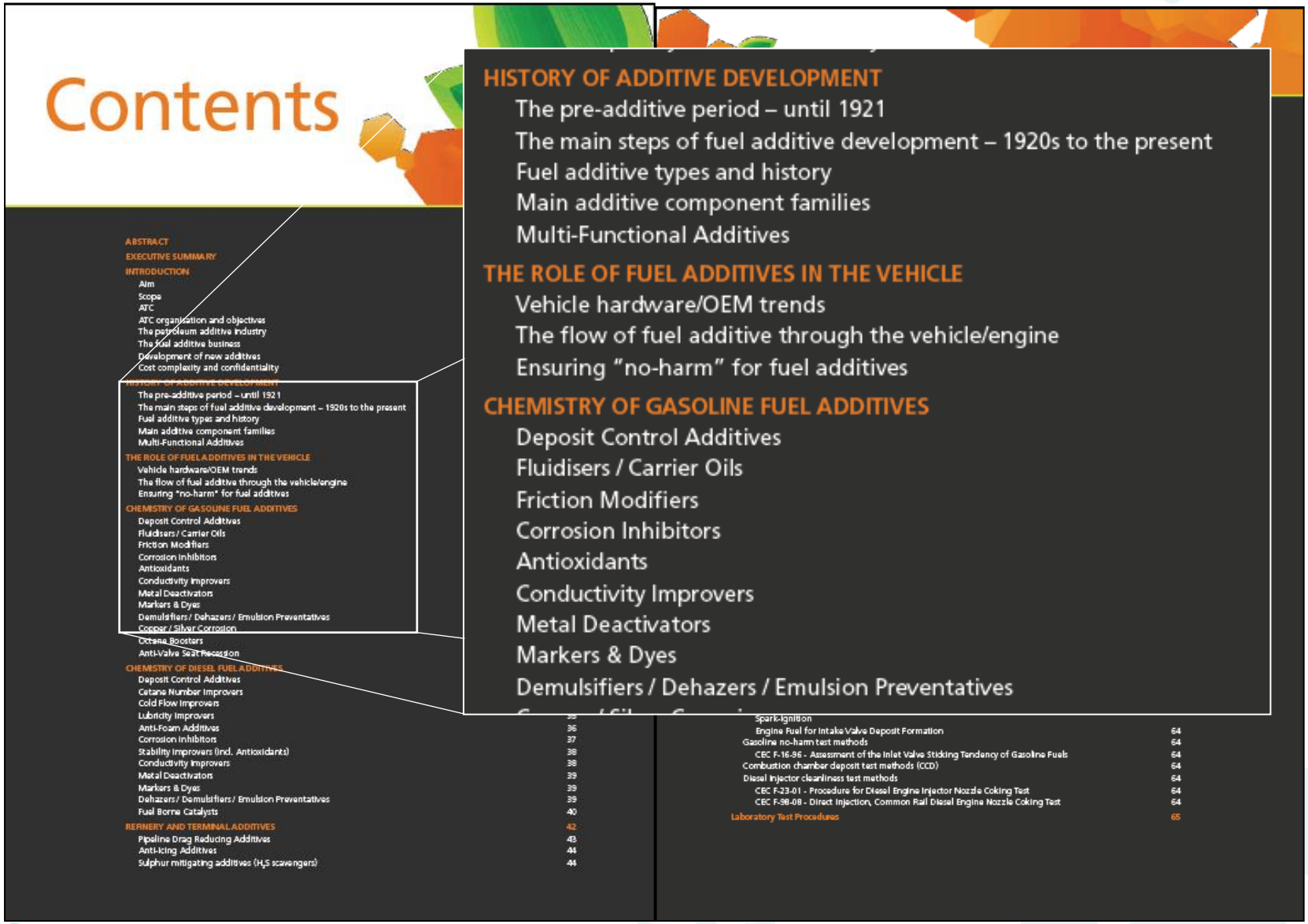


Chemistry of fuel additives

CHEMISTRY OF GASOLINE FUEL ADDITIVES

Deposit Control Additives

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.

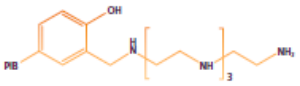
Intake system components

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.

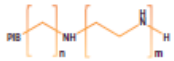
Deposit Control Additives are often referred to by the generic term **detergents** but their function is different to that of conventional detergents used for washing and cleaning purposes. Conventional detergents are controlled by European Regulation (EC) 648/2004 (the 'Detergents Regulation'), which 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.

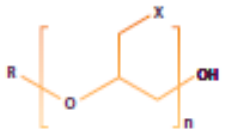
Consistent Approach for each additive type

- What they are
- What they do
- How they work

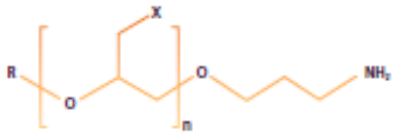
Use of diagrams and graphics

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)



Example of Demulsifier

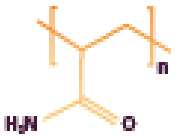
Phenolic resin alkoxylate

A=H or CH_3

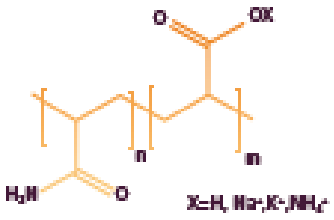
Where possible chemical structures have been included

Example of Pipeline Drag Reducing Additive

Polyacrylamide



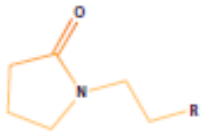
Partially Hydrated Polyacrylamide



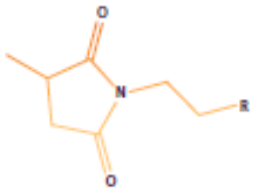
X=H, Na^+, K^+, NH_4^+

Examples Of Asphaltene Dispersant

Alkylpyrrolidone

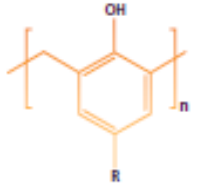


Alkylsuccinimide

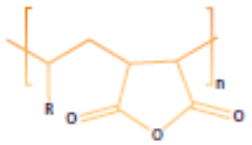


Examples of Ashphaltene Inhibitor

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



Alkene-maleic Anhydride Copolymer



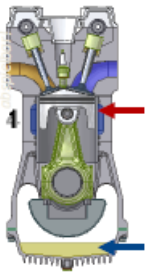
Technical but accessible

Friction Modifiers

Friction modifier (FM) additives are well known and
They are generally straight hydrocarbon chains wit
comprise amines, amides and their derivatives or ca
groups are attracted to metal surfaces such as cylin
relatively strong bonds, while the long hydrocarbo
The nature of the polar head group and the structu
on the contribution to friction reduction.

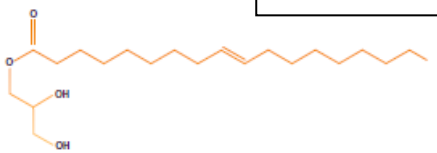
Friction Redution

How does a friction modifier work?



Example of Friction Modifier

Glycerol Mono-Oleate



Fuel Additives: Use and Benefits

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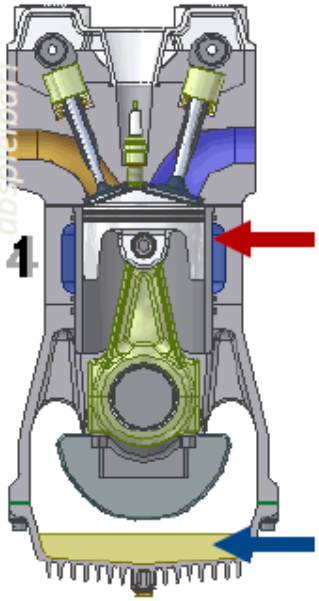
Friction Redution

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)

Informative but easy to read

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.

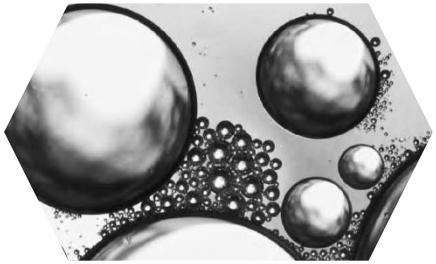
Lubricating oil interaction

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.

Fuel additives : use & benefits

Definition of a **fuel additive** :

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



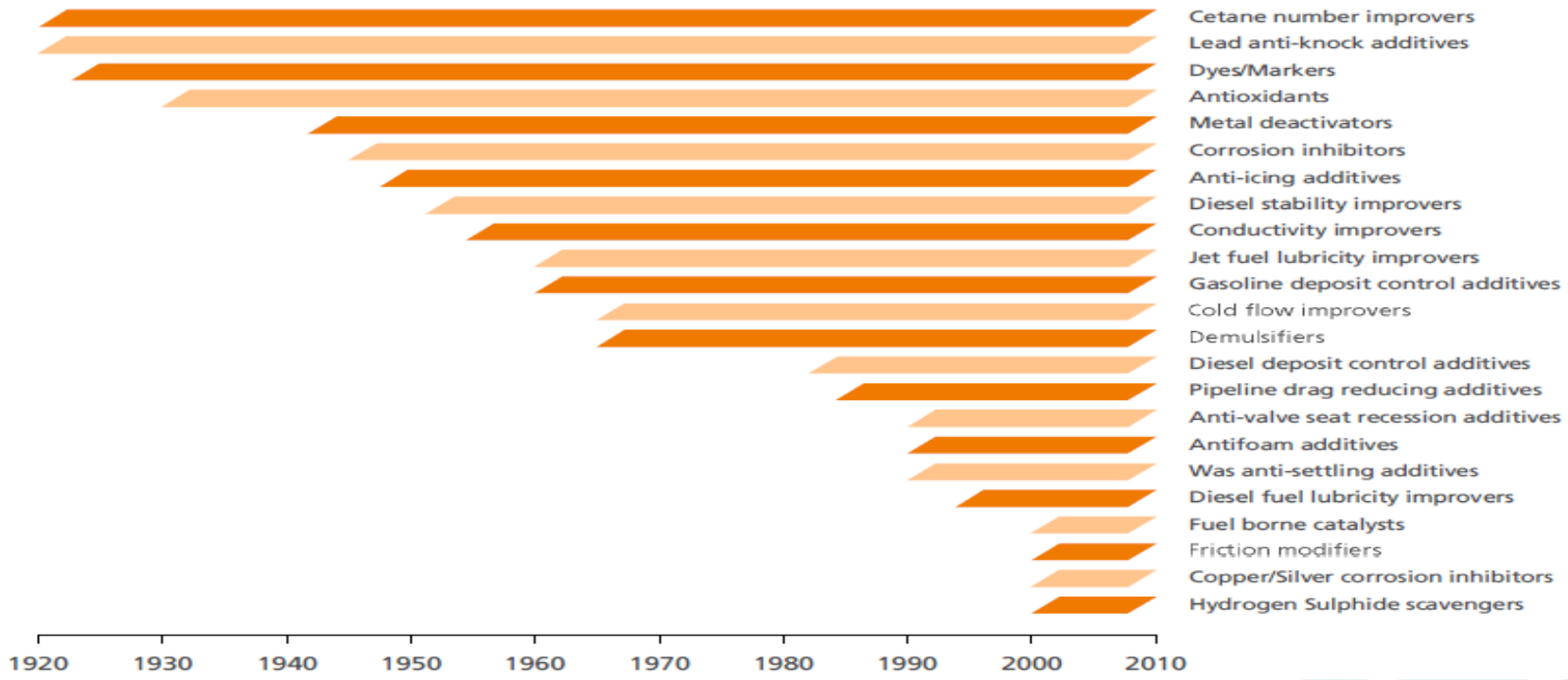
Fuel additives address the oil / energy / transportation industries in many ways :

- fuel in motor vehicles, aircrafts and marine vessels
- fuel / oil in power stations and domestic heating
- refinery process streams

Fuel additives : use & benefits

Fuel additives type and history :

- in the early stages, additives focussed on improvement of combustion properties of poorly refined cuts (octane, cetane)
- modern additives cover a broad spectrum of uses, including improved safety, operation and process, and end-use performance of fuels



Fuel additives : use & benefits

A comprehensive survey of **market data** collected from FAG members though CEFIC's statistical service (to ensure anonymity of the data), has estimated that :

The EU27 market for fuel additives is over 200,000 tons per annum and has a value of over €500 million

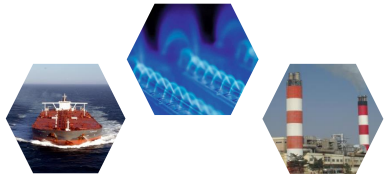
Over 95% of road retail fuels is treated with performance additives

All European refineries use additives in some capacity

ATC [2009-2011 figures]

Fuel additives : use & benefits

Typical components and uses :



	Refining / terminal	Transportation	Heating / Power gen.
Antioxidants	■	■	■
Stability improvers	■		■
Deposit Control	■	■	
Octane / cetane imp.	■	■	
Combustion imp.		■	■
Metal deactivators	■	■	■
Drag reducers	■		
Dyes	■	■	■
Lubricity improvers	■	■	
Friction modifiers		■	
Cold Flow improvers	■	■	■
Antifoam	■	■	
Corrosion inhibitors	■	■	■
Antistatic	■	■	
Dehazers	■	■	■
Reodorant		■	■

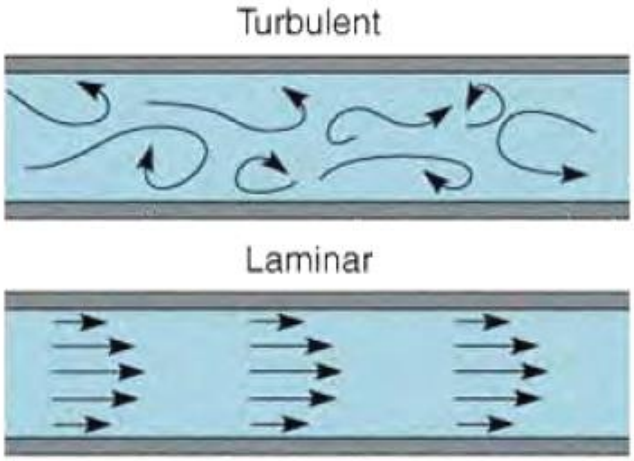
Fuel additives : use & benefits

Refining and Terminal additives

The use of additives provides **safer operations**, **improved processes** and **blending flexibility / optimisation**

Technical Problem

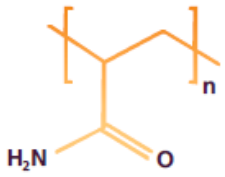
Pipeline pressure drop due to turbulent flow → lower throughput, higher pumping energy required



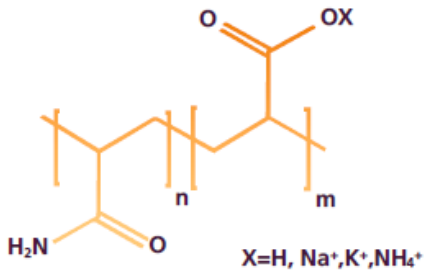
Additive / mode of action / benefit

DRAG REDUCERS / reduction of transverse flow / maintains throughput and pumping energy

Polyacrylamide



Partially Hydrated Polyacrylamide



Fuel additives : use & benefits

Refining and Terminal additives

The use of additives provides **safer operations**, **improved processes** and **blending flexibility / optimisation**

Technical Problem

Paraffin crystallisation

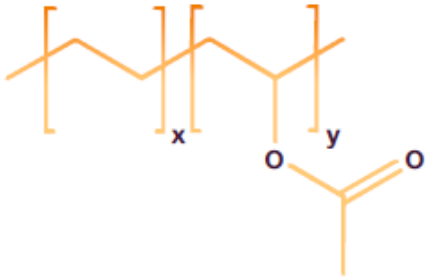
→ diesel fuel filter clogging

→ requires high amounts of specific cuts (e.g. kerosene) in the blending pool

Additive / mode of action / benefit

COLD FLOW IMPROVERS / delays crystal growth / lowers engine cold start temperatures

EVA: Ethylene Vinyl Acetate



Fuel additives : use & benefits

Refining and Terminal additives

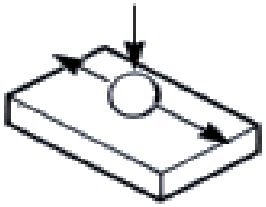
The use of additives provides **safer operations**, **improved processes** and **blending flexibility / optimisation**

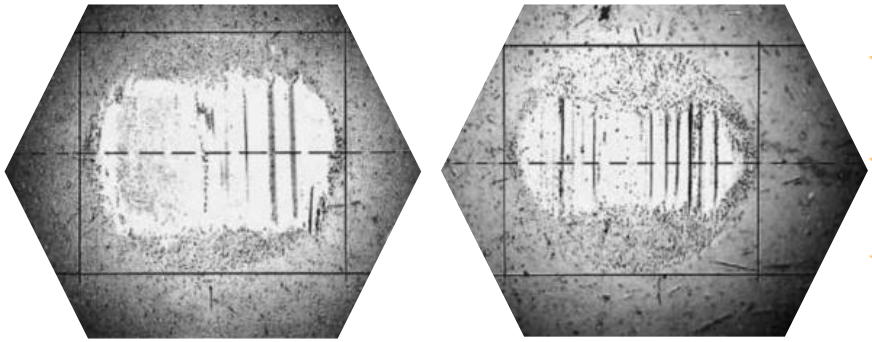
Technical Problem

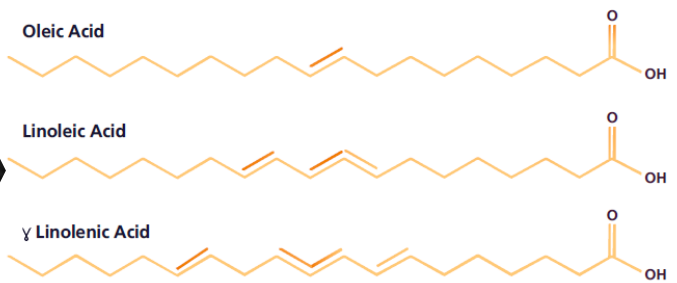
Desulphurisation reduces fuel polarity
→ vehicle fuel pump failure

Additive / mode of action / benefit

LUBRICITY IMPROVERS / protective film / high lubricity ULSD fuels







Fuel additives : use & benefits

Refining and Terminal additives

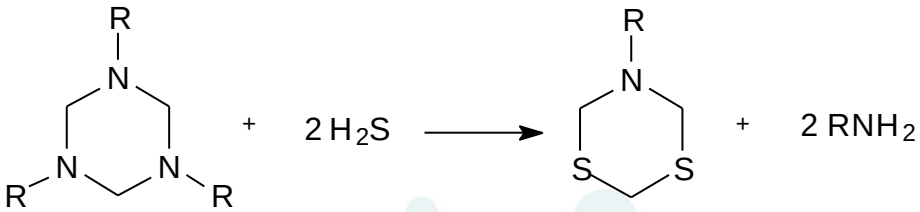
The use of additives provides **safer operations**, **improved processes** and **blending flexibility / optimisation**

Technical Problem

Entrainment of **H_2S** in hydrocarbons
→ potential personnel exposure

Additive / mode of action / benefit

H_2S SCAVENGERS / chemical reaction with H_2S into low hazard stable product / no H_2S release



Fuel additives : use & benefits

Automotive fuel additives

The use of additives maintains **original engine cleanliness** , improves **efficiency** and **protects engine parts**

Technical Problem

Gasoline inlet valve dirty-up

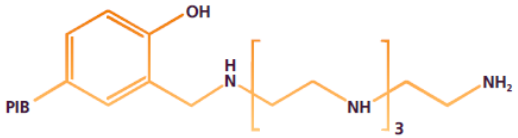
→ modified air/fuel ratio

→ lowered efficiency (consumption, emissions)

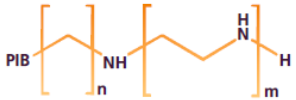
Additive / mode of action / benefit

DEPOSIT CONTROL ADDITIVES / protective film / maintains original engine performances and emission levels

PIB Phenol Mannich Amine



PIB Amine



Fuel additives : use & benefits

Automotive fuel additives

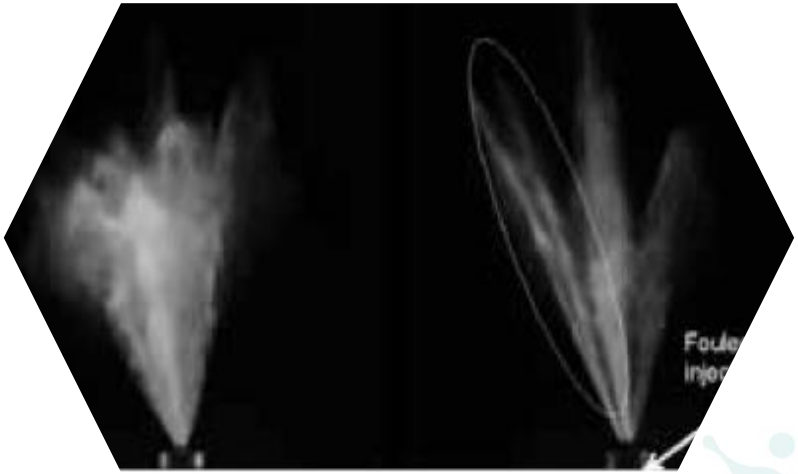
The use of additives maintains **original engine cleanliness** , improves **efficiency** and **protects engine parts**

Technical Problem

Diesel Injector fouling

→ **modified spray /combustion**

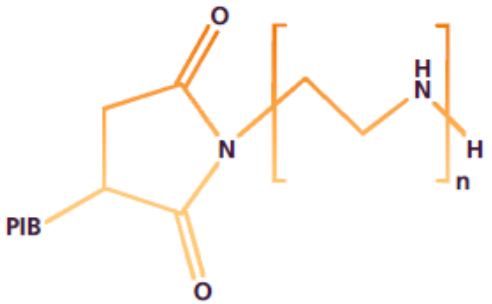
→ lowered efficiency (consumption, emissions)



Additive / mode of action / benefit

DEPOSIT CONTROL ADDITIVES / protective film / maintains original engine performances and emission levels

PIBSI: Polyisobutylene Succinimide



Fuel additives : use & benefits

Automotive fuel additives

The use of additives maintains **original engine cleanliness** , improves **efficiency** and **protects engine parts**

Technical Problem

Steel corrosion, rust formation
→ reduces parts lifetime
→ filters blocking

Additive / mode of action / benefit

CORROSION INHIBITORS / polar molecules forming protective film / reliable operation, long life

Fuel additives : use & benefits

Automotive fuel additives

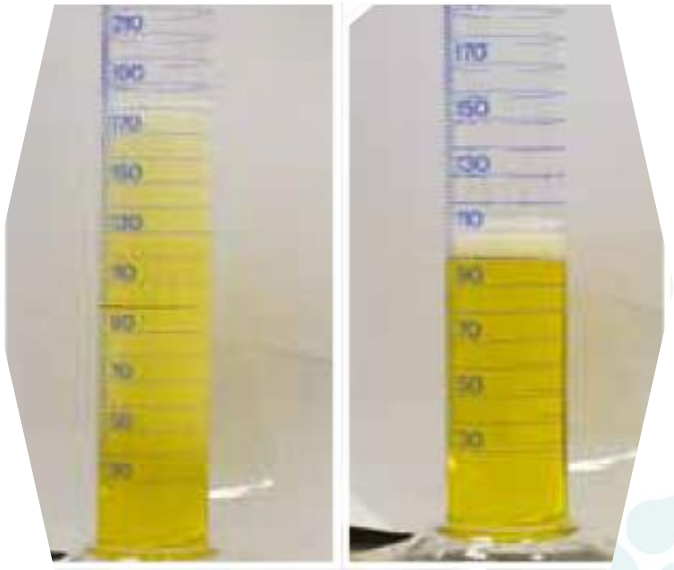
The use of additives enables **safer**, **easier** and **cleaner** operation

Technical Problem

Diesel foaming

→ filling overflow

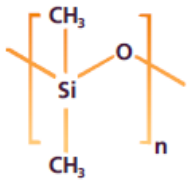
→ incomplete tank fill



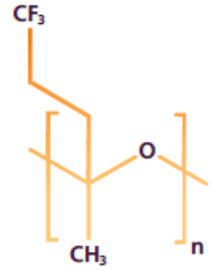
Additive / mode of action / benefit

ANTIFOAMS / reduce surface tension / lower foam volume and faster defoaming time

Polydimethylsiloxane



Modified Polydimethylsiloxane



Fuel additives : use & benefits

Automotive fuel additives

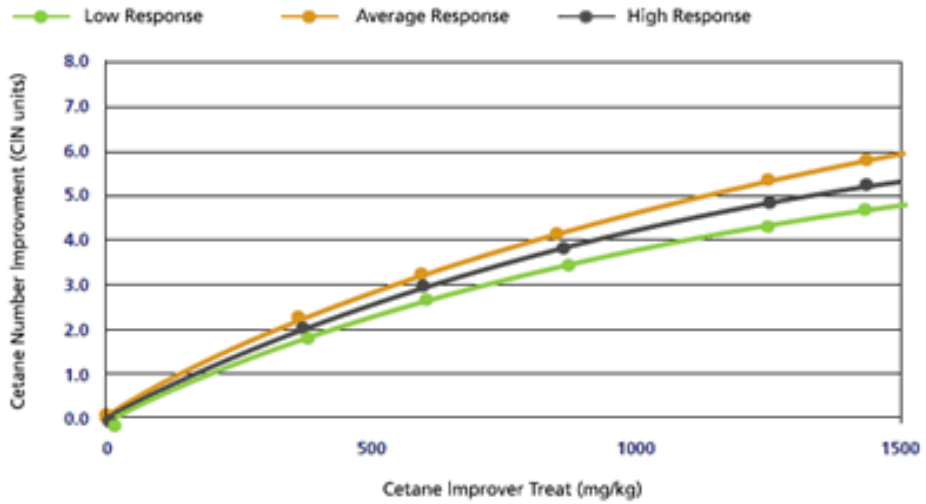
The use of additives maintains **original engine cleanliness** , improves **efficiency** and **protects engine parts**

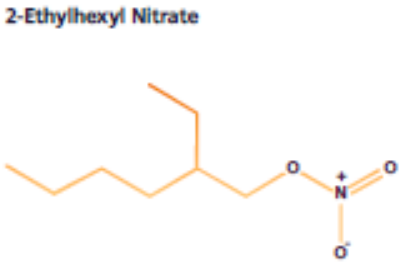
Technical Problem

Poor diesel combustion behaviour

Additive / mode of action / benefit

CETANE IMPROVERS / lowers ignition delay / more efficient combustion, lower noise





Fuel additives : use & benefits

Automotive fuel additives

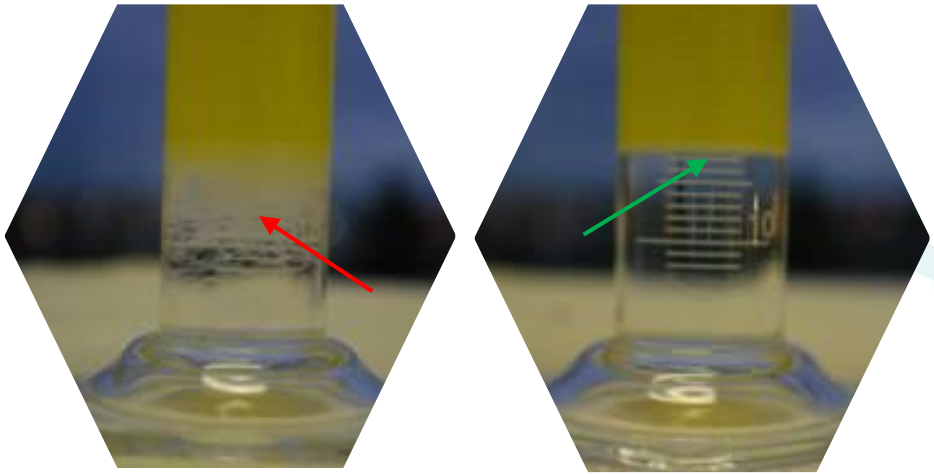
The use of additives maintains **original engine cleanliness**, improves **efficiency** and **protects engine parts**

Technical Problem

Water ingress in hydrocarbons
→ formation of emulsion
→ higher corrosion, fuel blocking, microbial growth

Additive / mode of action / benefit

DEHAZERS / break fuel-water interface / water separation



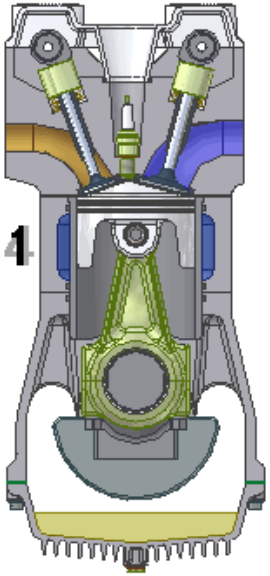
Fuel additives : use & benefits

Automotive fuel additives

The use of additives maintains **original engine cleanliness**, improves **efficiency** and protects **engine parts**

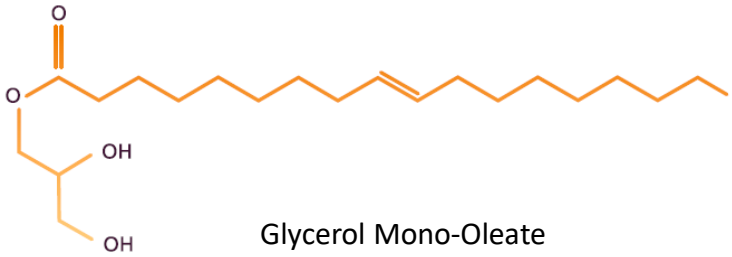
Technical Problem

Friction at the piston ring-cylinder wall interface
→ lowered efficiency



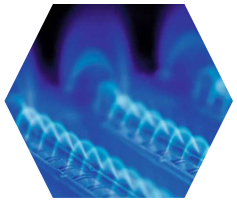
Additive / mode of action / benefit

FRICTION MODIFIERS / Surface coating to form a lubricating film / Enhanced efficiency (consumption, emissions, acceleration)



Glycerol Mono-Oleate

Fuel additives : use & benefits



Heating oil / marine / residual additives

The use of additives enhances **thermal stability**, improves **combustion properties**, disperses **impurities and** eases **product handling**

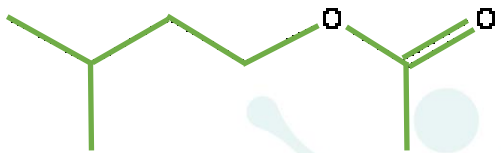
Technical Problem

Delivery and storing of domestic heating oil may lead to odour nuisance

→ Consumer complaints

Additive / mode of action / benefit

REODORANT / masks characteristic fuel smell / Easier product handling



Conclusions

Conclusions :

- Fuel additives offer a wide range of technical solutions to improve operation and performance in the oil / energy / transportation industries
- Fuel additives business (manufacture, R&D, use) represents a significant part of the European chemical industry
- ATC plays a **key role in the industry** by providing forum for all Petroleum Additives Companies within Europe to discuss developments of a technical or regulatory issue
- ATC will continue to participate actively in **industry test development** and maintenance work to assure quality and fairness in product performance testing
- ATC's new **Document 113** outlines the benefits of fuel additives

Contact

www.atc-europe.org

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