Lubricant Additives: Use and Benefits

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Technical Committee of Petroleum Additive Manufacturers in Europe

Contents

Abstract

The Technical Committee of Petroleum Additive Manufacturers in Europe (ATC) has carried out an analysis of the size and nature of the engine lubricants market in the 28 countries of the European Community (EU-28).

The first edition of this brochure was prepared in 1993 and revised in 2007. It was conducted to develop information which was not readily available, with the aim to show the contribution lubricant additives make towards the automotive industry, the consumer and the impact on the environment. This edition (2016) provides an update on recent additive developments and contains recent data on the lubricant market.

This document describes the chemistry and functions of lubricant additives, as well as their role in the development of advanced engine systems. Product health and safety aspects are reviewed. The benefits of additive technology towards engine operation and end-users are explored.

Executive Summary

"Lubricant 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 fourteen specialty chemical manufacturers, including some household names, which together are responsible for the production and supply of almost all the additives used in lubricants. Such additives encompass applications for lubrication of passenger car diesel and gasoline engine lubricants (PCMO - passenger car motor oil) and in truck, coach and bus diesel engine lubricants (HDEO - heavy duty engine oil). The document demonstrates the contribution made by lubricant additives in these applications to the consumer, industry and the environment, through their ability to optimise desirable lubricant properties while suppressing unwanted ones. In this context, the term 'lubricant additive' is reserved for a chemical substance or prepared mixture, added to base oil, in concentrations typically ranging from 0.05 to 30 wt.%, to impart or enhance the chemical and physical properties for usage in a combustion engine.

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 worldwide turnover of about €11,700 million, (€3,600 million in Europe) and research and development (R&D) spending in 2014 of €600 million (€240 million in Europe). The industry has 12,000 direct employees worldwide (3,800 in Europe), maintaining over 100 R&D and manufacturing sites globally (35 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 lubricant 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 lubricants additives industry, a challenge which nevertheless the industry has shown it can meet since its infancy in the 1930s when in order to improve the cold temperature operability of base oils, pour point depressant additives were first introduced. Further developments have occurred in almost every decade, for example, anti-wear additives evolved in the 1940s in response to higher load conditions experienced by engines developed during that period, or detergent chemistries were developed which provided anticorrosion / antirust performance and kept engines clean by solubilising deposits formed by the incomplete combustion of fuel. In a further example, a major development during the 1950's was the development of viscosity modifiers which enabled year round use of a lubricants and the introduction of multigrade viscosity classifications. In more recent decades the focus of innovation within the lubricant additive industry has been around maintaining engine durability in the context of ever challenging emission reduction and fuel economy targets, resulting in the need to reduce levels of the more traditional anti-wear and detergent chemistries which can impair the effectiveness of exhaust after treatment devices, developing additive chemistries and formulation techniques to replace them as well as driving the move towards lower viscosity lubricants and the introduction of supplementary friction reduction additive chemistries.

"Lubricant Additives: Use and Benefits" details a wide range of additives employed in PCMO and HDEO oils. 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 use and benefits of lubricant 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. The technical aspects of lubricant additives are well covered, with over 40 references cited, thus providing an excellent basis for further study by those interested in increasing their understanding of this technology-driven branch of science.

Introduction

This document has been prepared by a task force, consisting of representatives of 4 major additive suppliers, on behalf of ATC - The Technical Committee of Petroleum Additive Manufacturers in Europe.

The petroleum additive industry develops technologies and materials for the supply of service products for engines and motor vehicles. This is in co-operation with the petroleum and automotive industries, and end-users. ATC defines engine lubricant additives as:

A chemical substance or prepared mixture, added to base oil, in concentrations typically ranging from 0.05 to 30 wt%, to impart or enhance the chemical and physical properties for usage in a combustion engine.

While the activities of the industry are very well known to its customers in the oil industry and to its indirect customers in the motor industry, 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 feel a need to know more about our industry and particularly its benefits towards the consumer and its impact on the environment.

Introduction

Aim

The aim of this document is to introduce ATC, to explain how the association operates, and to show the contribution lubricant additives make towards industry, the consumer and the impact on the environment.

The purpose of ATC is to ensure communication with all industry, customer, original equipment manufacturer and governmental stakeholder groups. This paper hopes to provide relevant data of a technical and regulatory nature to allow representatives to focus on future priorities of lubricant technology developments.

Scope

This document confines itself to automotive engine oil additives, their chemistry and the benefits they provide. Automotive engine oil additives comprise those used in passenger car diesel and gasoline engine lubricants (PCMO - passenger car motor oil) and in truck, coach and bus diesel engine lubricants (HDEO - heavy duty engine oil). This study is limited to products used in four-stroke internal combustion engines in road vehicles, which represents most of the engine oil additive use in Europe. Other additive markets including agricultural vehicles, railway, off-highway construction, two stroke engines and stationary engines are less well defined and are excluded from this study.

The total consumption of lubricant additives by the 28 European Community members (as of April 2015) has been taken into account., The top five lubricant markets in Europe represent nearly two-thirds of the region's demand (Kline & Company 2013). Volumes of ACEA approved lubricants sold outside the EU in neighbouring countries (i.e. Turkey and Russia), increased significantly during the last five years.

ATC

The Technical Committee of Petroleum Additive Manufacturers in Europe (ATC) was established in 1974 for member companies to communicate on matters of mutual interest. In 1979, ATC became affiliated as an industry sector group of Cefic, a federation of associations representing European chemical manufacturers. The current members are shown in Table 1[1].

Table 1. Members of ATC

AkzoNobel	Eurenco
Afton Chemical	Evonik Oil Additives
Baker Hughes	Infineum
BASF SE	Innospec Fuel Specialties
Chemtura Corporation	Lubrizol
Chevron Oronite	Rheinchemie
Croda	Total ACS

Membership is open to all additive companies which manufacture petroleum additives, or have comprehensive test facilities in Europe. Further information about ATC can be found on the website www.atc-europe.org.

ATC Organisation and Objectives

The ATC organisation comprises a main committee and sub-committees responsible for, amongst others, Health & Safety Legislation, Lubricant Performance Testing, Fuels Additives and Quality Monitoring. In addition, the Technische Vereinigung für Mineralöl-Additive in Deutschland e.V. (TAD) co-ordinates activities for ATC in Germany.

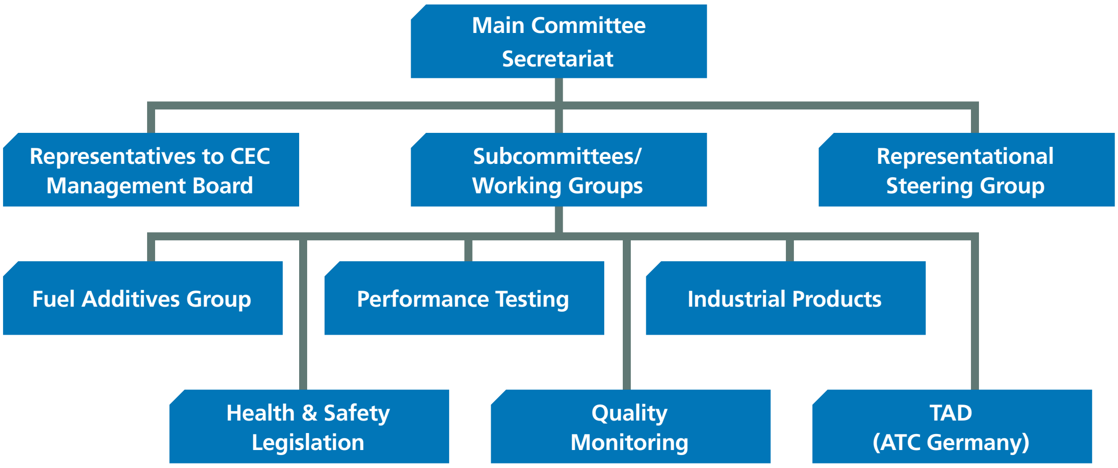


Figure 1. ATC Organisation

ATC aims to provide a forum for petroleum additive companies in Europe to discuss developments of a technical or regulatory nature:

- To ensure that products and technologies delivered are “fit for purpose”, meeting or exceeding industry standards defined by original equipment manufacturers, customers, and lubricating oil quality surveillance programs.
- To work together with regional and international petroleum, automotive, and industrial industry groups.
- To initiate or participate in appropriate technical work in support of industry objectives.

For example, ATC has developed descriptive terminology for products to assist legislators by providing standardised industry reporting whilst protecting confidentiality. Technical data are shared to provide accurate labelling of products where required. ATC Health and Safety Legislation Sub-Committee works closely with the REACH (Registration Evaluation and Authorisation of Chemicals) Steering Committee monitoring the implementation process and wider publication and communication of advice on safe handling of lubricant additives.

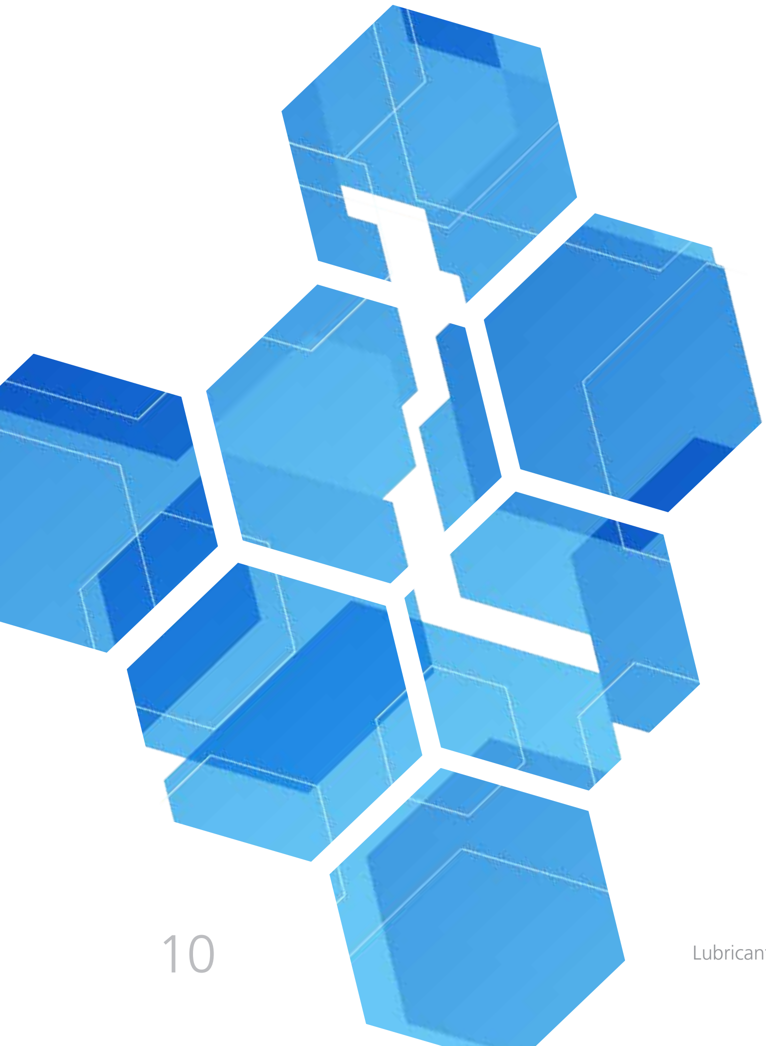
By communicating with associated industries and technical bodies (e.g. ACEA, Association des Constructeurs Européens d’Automobiles; CEC, Coordinating European Council for the Development of Performance Tests for Lubricants and Engine Fuels; ATIEL, Association Technique de 1’Industrie Européen des Lubrifiants; CONCAWE, The Oil Companies’ European Organisation for Environmental and Health Protection) technical issues can be pursued and developed for mutual interest. The ATC also provides a focal point for the industry to communicate with government bodies.

The Petroleum Additive Industry

The petroleum additive industry is a research and development intensive industry and its products are marketed solely to industrial users. Some key facts (from 2014) about the petroleum additive industry are:

- World-wide the industry spends about €600 million/annum on research and development, of which €240 million is spent in Europe (EU-28).
- World-wide the industry has a turnover of about €11700 million of which the European market is about €3600 million.
- The industry employs directly about 3800 people in Europe and about 12000 globally.
- The industry operates more than 35 research and development establishments and manufacturing sites in Europe, and more than 100 globally.
- The petroleum additive industry in Europe is a major exporter.

ATC member company objectives include the development of additives for fuels and lubricants in co-operation with the oil and motor industries which meet present, and future performance and environmental legislation cost-effectively and which solve or mitigate both existing and anticipated problems of vehicle or engine operation.



European Engine Lubricant Additive Industry Profile

European Crankcase Lubricant Additive Industry Profile

Sources of Data

Compared to the previous version of this document of 2007, the EU has expanded its membership from 15 to 28 countries. Information about the size of the engine oil additives market in Europe was obtained by requesting sales data from individual ATC members. These data were submitted anonymously to Cefic (The European Chemical Industry Council) which provided a detailed breakdown into components of the top 80% (by volume) of additive packages sold in the EU-28 countries, both for passenger car and for truck, coach and bus (hereafter referred as "commercial vehicle") market segments. From these data the total additive volume has been obtained, which together with the additive treat rate gives the total engine lubricant volume in the EU-28 countries. This total figure is divided into passenger car use - PCMO - (1370 kilotonnes/year) and commercial vehicle use - HDEO - (1040 kilotonnes/year) and is shown in Table 2.

Table 2. Estimated Engine Lubricant Market

Estimated engine lubricant market (kilotonnes) based on:	Passenger Car Engine Oils	Heavy Duty Engine Oils	Total
ATC member data (2014 – EU-28)	1370	1040	2410
Kline report (2014 – EU-28)	620	800	1420
ATC Document 49 (2005 – EU-15)	1270	1330	2600
EuropaLub report (2004 – EU-15)	913	744	1657
ATC Document 49 (1993 – EU-12)	1200	1400	2600

As can be seen there is a discrepancy between the sources of data. Estimating the EU-28 engine lubricant market based on additive sales leads to a higher estimate, 2,410 kilotonnes, than the lubricant market based on the Kline & Company report, 1,420 kilotonnes. The Kline & Company report is based on lubricant sales in the 28 EU countries. This survey ignores additives that are produced in the EU-28 and exported for blending outside EU and also finished lubricant exports.

The 2014 Kline & Company and 2004 EuropaLub data clearly reflect that finished lubricant volumes in Europe are steadily declining, a trend that has been apparent for a number of years. This decline is mainly seen in the passenger car segment and is largely attributed to reductions in oil sump volumes and oil consumption rates in modern engines. Since the EU lubricant market has grown from 12 to 28 member states the actual decline is even larger. Comparing the ATC member data from 1993, 2004 and 2014 shows the total European additive volumes are relatively stable. It is interesting to note that the passenger car engine oil market has shown an increase in volume which is offset by a decreasing volume in the heavy duty engine oil market. Since these volumes are based on additive sales these trends this can be explained by increasing additive treat rates in modern passenger car oils as well as a lesser emphasis on extending drain intervals. This in contrast to commercial vehicles where operating costs are a greater concern.

Lubricant consumption per EU country is shown in Figure 2 [2]. The DACH countries (Germany, Austria, Switzerland), UK and France account for about 50% of the EU lubricant sales.

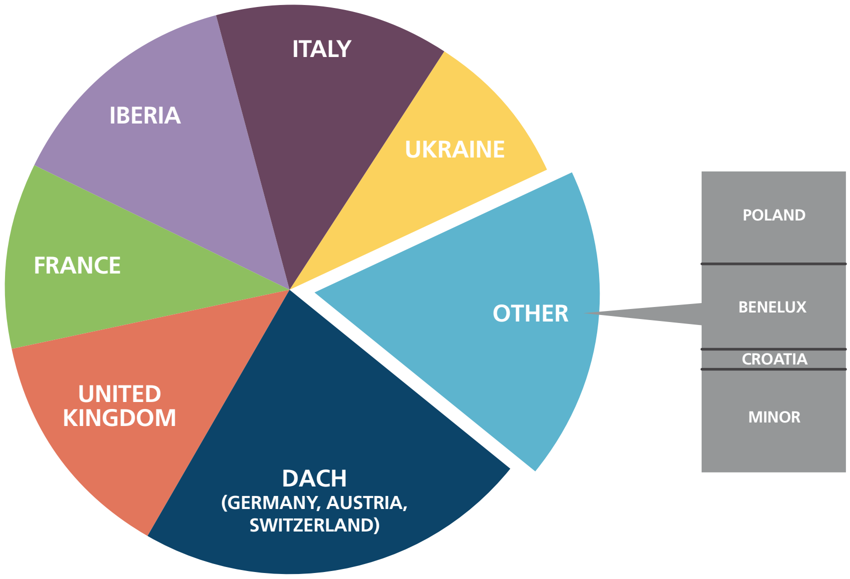


Figure 2. Europe Lubricant Consumption by Country (2014)

The Automotive Engine Lubricant Additive Business

The lubricant marketer identifies the necessary product characteristics to meet the consumer needs. Commercial requirements, together with technical targets, are evaluated by the additive companies who typically manage the development of a new lubricant.

In Europe, the technical performance requirements of finished lubricants are specified by

- ACEA (Association des Constructeurs Européens d'Automobiles- European Automobile Manufacturers' Association)
- API (American Petroleum Institute)
- OEMs (Original Equipment Manufacturers)

The petroleum additive suppliers formulate and test combinations of additive components in base stocks to achieve industry and OEM standards of performance. Various parameters, such as wear, friction, oxidation resistance, and engine cleanliness, are evaluated in standard laboratory and engine "rig" tests before the new lubricant (containing the additive package) is offered for sale to the customer. Evaluation of the prototype lubricant in a controlled field test can be part of the OEM approval process. In many cases these test data will be presented to an industry body or an OEM for lubricant approval.

On completion, the new lubricant (containing the qualified additive package) will be offered for sale by launching a promotion campaign stating the industry claims and differentiating performance benefits. Proprietary details of its composition are generally not disclosed.

European Crankcase Lubricant Additive Industry Profile

Automotive engine lubricants sold in the customer market contain performance additives, at total concentrations of typically 10 - 30%. Additives are added to improve the performance of petroleum-derived base oils necessary for efficient operation and prolonged engine life. Modern lubricants contain a combination of various additives to meet the most severe oil requirements which are impacted by engine design, operating conditions, legislation, and source of supply and processing methods of the base oil stocks. Additive components of different chemistries are used, at concentrations (in the finished lubricant) from 0.005% to more than 10%. The particular combination of additive components used in an automotive engine oil is generally known as an additive package.

Development of New Additives

New additives are developed to meet changes in engine design, environmental legislation or OEM requirements. For example, advanced lubricant additives can help to improve fuel efficiency and to reduce CO_2 emissions from cars and commercial vehicles by reducing friction. To prolong the lifetime and maintain the efficiency of exhaust car emission reduction devices, some modern engine oils are Low SAPS (Sulfated Ash, Phosphorus and Sulfur). New additives have been developed which maintain the functionality and engine protection while reducing the amount of conventional metallo-organic active additive components. To ensure additive formulations meet these requirements, new or existing engine tests, testing of physical characteristics or performance properties are prescribed by industry bodies (e.g. ACEA) and OEMs.

Cost, Complexity and Confidentiality

The costs of engine testing are high because they have to be performed by industry certified testing facilities to ensure statistically valid data. The tests are run under controlled conditions using an engine and fuel with specified tolerances. The engine test development costs for an engine lubricant, suitable for use in today's diesel and gasoline engines, can range between 0.5 and 5 million euros. This presumes the existence of a considerable amount of in-house data and formulation skills. The latter are extremely important as many of the requirements are conflicting (i.e. use of an additive to improve Test A could make Test B worse). Oil development costs, sponsored by lubricant additive companies, show a substantial increase when OEM specific tests or extensive field tests in vehicles are needed to guarantee its performance.

To meet the ever-changing needs of the engine designer and of the consumer, often enforced by more strict environmental legislation on vehicle emissions, the additive industry puts a major effort into developing enhanced products. Many of these developments fail to meet their technical targets, but some pass all the tests and become commercial products. The additive industry spends more than €240 million/ year in EU-28 on new developments. A single component can cost between one and ten million Euros to develop, test, register and manufacture on a commercial scale. Therefore, it can take ten to fifteen years to see a return on the investment. The cost of compliance with health and safety legislation has risen over the years, and has increased further now REACH is being implemented.

Petroleum additive companies require considerable financial investment and the innovative skill of their employees to develop additive components and packages. They are selling performance products and not commodities. Suppliers do not disclose the composition of additive packages, as the results of their investment in research and development would be available to anyone having access to the composition. If compositions were disclosed, the incentive for companies to innovate would disappear.

A lack of innovation could have serious consequences. Today's engines will not function on yesterday's oils. Tomorrow's engines will need new additive packages. Improvements in fuel economy alone will require additive developments to meet the challenges of higher engine temperatures and lower friction requirements as well as compatibility with new materials.

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 always be readily patentable. Therefore, many such inventions are treated as proprietary compositions without additional patent filing.

To ensure continued investment in R & D and innovation 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 ensure the safe use of member companies' materials consistent with protecting intellectual property, they work closely within the REACH Consortium on the registration of additives and legislative requirements for disclosure of hazardous materials on the Safety Data Sheet (SDS).

History of Lubricant Additive Development

Introduction

The automobile industry is the major user of lubricants. Engine designs have been continually improved to enhance performance, increase efficiency, and at the same time meet environmental emission regulations.

Engine oils lubricate the moving parts and protect components of an engine. Engine oils are an essential contributor to the reliability and durability of modern internal combustion engines.

Engine oils must be thin enough when a cold engine is fired up to be able to flow immediately from the oil sump in the bottom to lubricate vital engine components in the top part of the engine. Most of the engine wear occurs at start-up before the oil can reach out to all the engine parts.

The provision of a lubricating film between moving parts is a vital function. Engine oils must prevent the metal-to-metal contact that will result in wear. Full-film lubrication occurs when the moving surfaces are continuously separated by a film of oil.

When engines heat up the thickness of the engine oil film has to stay between specified limits to be able to provide adequate engine lubrication. The viscosity of the oil is the measure to specify these limits. The viscosity of the oil changes as it becomes contaminated during the use of the engine. Dirt, oxidation and sludge can increase the viscosity of the oil while fuel dilution will reduce the viscosity. Engine oil formulators keep these effects in balance and protect the engines with modern engine oils throughout the drain interval.

Internal combustion engines do not burn all the fuel completely. Some of the partially burned fuel experiences complex chemical changes during combustion to form sludge and varnish deposits on engine parts. Combustion deposits act as a heat barrier and as a result pistons, rings, spark plugs, and valves are not properly cooled. Sludge build-up may clog oil passages which reduces oil flow. Varnish build-up interferes with the proper clearances, restricts oil circulation, and can cause failure of vital engine parts.

Engine combustion by-products and wear debris are constantly generated. Modern engine oils handle these contaminations and hold them in suspension until they are removed by the oil filter or the next oil change.

The cooling system mainly controls the upper part of the engine whereas the core parts are generally cooled by the engine oil. Combustion engines have ideal operation temperature regimes with lower and upper limits. When the engine is cold and the engine is started up the engine oil acts to transfer heat and helps reach the lower limit of operability as quickly as possible. When the engines reach their upper limit the oil acts as a coolant.

Modern combustion engines run hotter than earlier generations and the cooling and heat transfer performance of engine oils is even more important than it was in the past.

Because of the rapidly moving parts in an engine, oil is constantly being mixed with air or other gases and this can lead to air entrainment and a tendency to form foam. Foam is not a good conductor of heat, and will impair the cooling of the engine parts. Also, foam interrupts the load carrying capability and the lubricant flow. This could result in excessive engine wear. Modern engine oil formulations are designed to prevent air entrainment and the build up of foam.

Rust and corrosion protection of a wide range of engine parts is also provided by the use of inhibitors. The challenge is the tremendous variety of different materials in engines that engine oils have to protect. Rust and corrosion inhibitors protect all these different engine parts from chemical attack caused by a wide variety of contaminants.

History of Lubricant Additive Development

To achieve the environmental emission limits that legislation is demanding, engine designers have to make use of different components in after treatment systems that operate at the same time. These are mainly catalytic converter and particle filters. Modern engine oils must be designed with protection of exhaust after-treatment as a necessary pre-requisite.

In addition, modern engine oils are formulated with latest friction or viscosity modifying properties in order to aid fuel economy. This is to enable reduction of friction between moving surfaces and providing favourable improved viscosity profiles that lead to higher thermal efficiency.

Frequently engine designers reach chemical or physical limits that they can only overcome when they are supported by increased performance from engine oil formulations. The lubricant is in many cases no longer only a commodity but rather an important design element of new engine development programs.

Research is ongoing to formulate lubricants to meet the demands of latest engine designs. Beside their main task modern lubricants must perform several additional functions to cover the needs of modern engines that will be explained more in detail in the chapter "Chemistry of Lubricant Additives".

Base Oils

Engine oil is basically a combination of base oil and additives. Additives are necessary to provide performance beyond what base oils alone are able to offer. Base oils can be considered as a carrier for the additive and a cooling medium even when the base oils also influence the performance of formulations.

The demands based on engine development programs have led to a wide range of base stock classifications that are covered by 5 Groups. These differences are defined by on saturates level, sulfur content and viscosity index (VI) properties of the oil (Table 3).

Table 3. Base Oil Groups and Characteristics

Group	Description	Sulfur	Saturates	V1
I	Crude oil is distilled, refined physically with solvents, and may also be hydrofinished, to leave a base stock and by-products.	>0,03%	<90%	80-120
II	Crude oil is distilled and chemically refined by hydrogenation, to leave a base stock with fewer by-products.	<0,03%	>90%	80-120
III	Cruide oil is distilled and refined by severe cracking and hydrogenation, to produce a higher VI base stock and even fewer by-products.	<0,03%	>90%	>120
IV	PAO-polyalphaolfins are chemically synthezised base stocks with increased VI compared to Group III stocks.	<<0,03%	>>90%	>>120
V	All base stocks not classified in other groups, including vegetable oil, derived base stocks, esters, diesters, glycols, etc.	<<0,03%	>>90%	>>120

Lower Sulfur

Higher VI

Purer

Higher flash point

Traditional lubricant base stocks are derived from distillation and solvent extraction of crude oil, sourced world-wide. Alternatively the crude oil may be more highly refined using processes that include cracking and hydrotreating to produce higher quality base stocks. Some high performance formulations incorporate chemically manufactured hydrocarbons such as polyalphaolefins (PAO) and esters. In recent years the investment in developing the technology to convert natural gas to liquids on a commercial scale has come to fruition with the introduction of a range of Gas to Liquid (GTL) products including materials used for transportation fuels and lubricant base oil. GTL base oils have a very high viscosity index, low sulfur and low volatility and can be used in high quality lubricants when formulated with appropriate lubricant additives. Current GTL base stocks generally fit into API Group III and with their very high viscosity index (>130) are often marketed as Group III+.

Base stock properties can differ markedly depending on the source of crude and the refining process. Lubricant additive technology provides the necessary enhancement to these base fluids to achieve OEM and industry standards of performance. This increase in performance and value of formulated lubricants permits more effective use of petroleum resources.

Over the last almost 100 years a number of chemical additives have been developed to enhance base oil properties, overcome their deficiencies and provide the new performance levels required by the technological evolution of engines and by the latest regulations.

History of Lubricant Additive Development

The Pre-Additive Period – Until Early 1930s

Until the 1930s engine oils contained no additives, comprising only base oils. Oil drain intervals were necessarily very short (1,500 km or less) to ensure adequate lubrication. The existing oil classification system, first adopted in America in 1911 by SAE (American Society of Automotive Engineers) was related only to oil viscosity and not performance.

However, due to increasing consumer demands and economic pressures, internal combustion engines became more sophisticated. Engine oils were becoming increasingly stressed and challenged in their performance reserves giving rise to a need for additives.

The Main Steps of Lubricant Additive Development - 1930s to the Present

Figure 3 gives a chronological view of the development of the main additive families[5-15]. These developments have been driven by new specification demands imposed by engine design changes, which in turn are a response to consumer demand and emissions requirements.

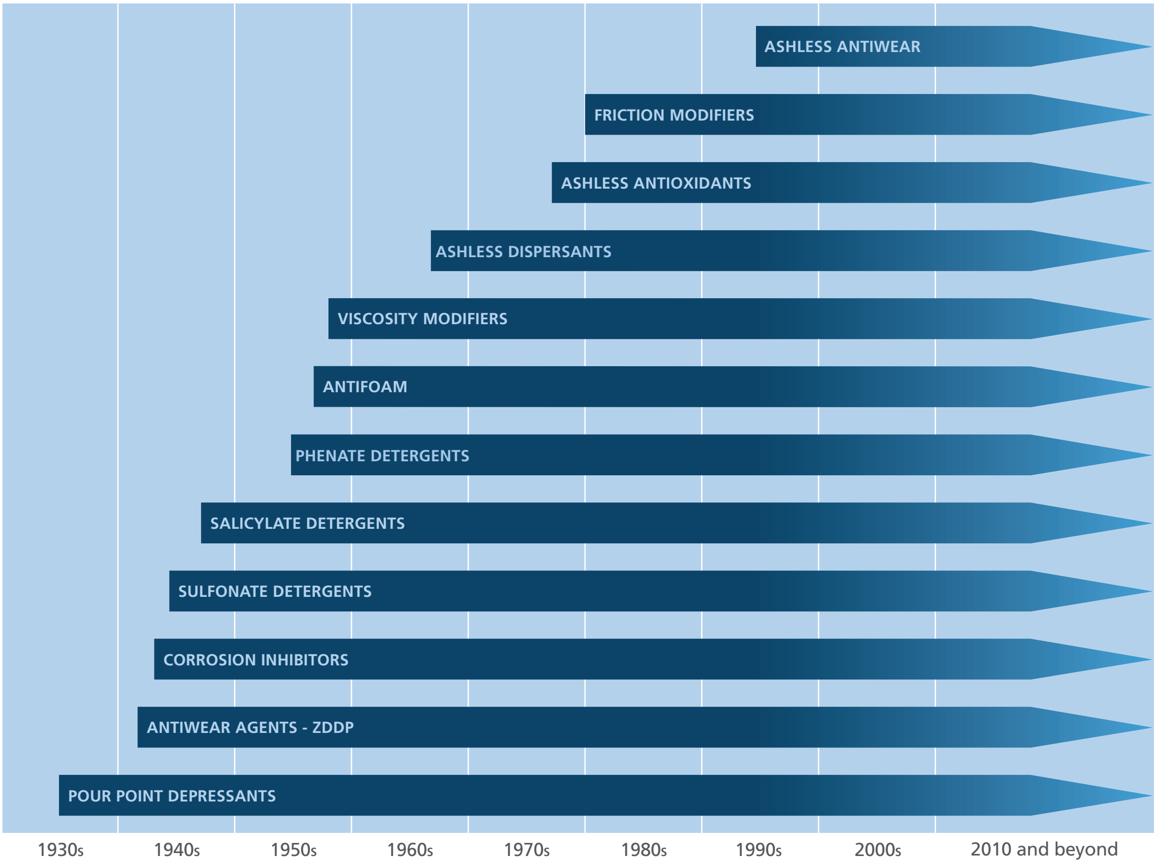
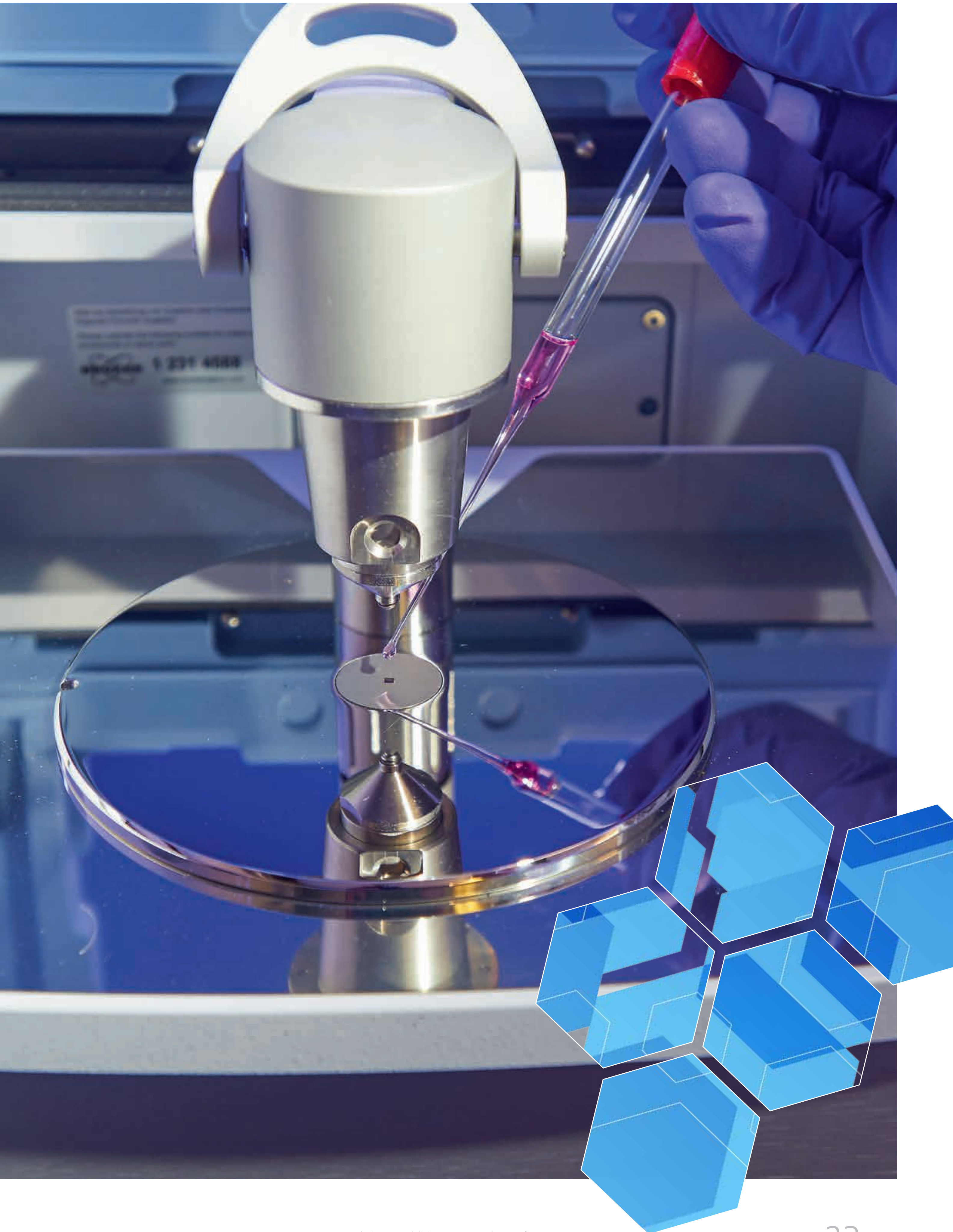


Figure 3. Timeline of Main Lubricant Additives

Further diversification within each additive family continues. Development is mainly driven by new lubricant specifications, which in turn are driven by evolution in engine design to meet emissions legislation and increasing consumer demands like fuel economy.



Chemistry of Lubricant Additives

Introduction

Additives perform a wide variety of functions within engine lubricants. This includes:

- Protection of engine surfaces. Many additives have anti-wear, anti-rust or anti-corrosive properties, which in combination prevent damage to coatings and surfaces within the engine.
- Modifying the physical properties of the lubricant. Viscosity modifiers and pour point depressants are used to maintain the desired physical properties (most importantly viscosity) at all temperatures and running conditions. This ensures adequate flow and viscosity of engine oil in all circumstances.
- Prevent and control the effects of engine deposits. Additives with antioxidant properties help slow the oxidation process the build-up of undesired engine contaminants and oil thickening. Dispersants and detergents aid in keeping engine surfaces and parts clean alongside controlling deposit mediated engine oil thickening.
- Increased fuel economy. Additives with friction or viscosity modifying properties can also aid fuel economy. This is via the reduction of friction between moving surfaces or providing favourable viscosity profiles that can lead to improved efficiency.

Although most additives have a primary function (e.g. dispersants control soot and sludge deposits), many also have secondary desirable characteristics that increase overall lubricant performance. For example it is well known that detergents neutralise acids which help prevent corrosion, aid in keeping engine parts clean and some detergents also have antioxidant properties.

Even though additives are classified into different chemical groups, their functions are varied. Using formulation expertise, additive companies can create an overall additive product that meets the overall performance required from the engine lubricant.

Oil Solubility

Most lubricant additives are oil soluble materials. In fact, many are prepared using oil as a solvent. For storage stability and handling reasons, many additives are made as 45 - 90 wt. % concentrates of active material in oil. Polymeric additives used as viscosity modifiers can be diluted even more to facilitate handling.

Additive molecules typically have long, oil soluble, hydrocarbon (non-polar) tails and smaller, hydrophilic (polar) head groups (Figure 4). Since the two parts of the molecule have different solubilities in oil, additives therefore tend to exist colloidally as inverse micelles.

Figure 4. Schematic Representation of a Polar Additive Molecule

Detergents

Oil-soluble detergents are formed by combining a polar substrate with a metal oxide or hydroxide.

The polar substrate is made up of two parts. The hydrocarbon tail or oleophilic group acts as the solubiliser enabling the detergent to be fully compatible and soluble in the base stock. The polar head contains the acidic group which reacts with the basic metal oxides or hydroxides.

Detergent polar substrates types fall into three main classes.

Sulfonates

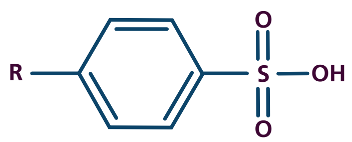


Figure 5. General Structure of a Sulfonate Based Detergent

Phenates

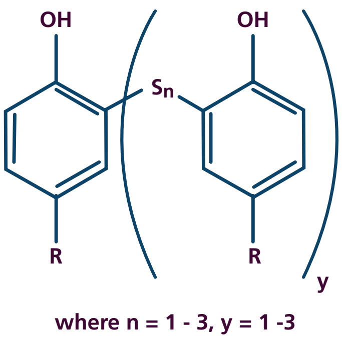


Figure 6. General Structure of a Phenate Based Detergent

Salicylates

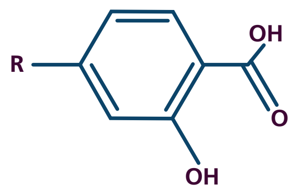


Figure 7. Typical Structure of a Salicylate Based Detergent

Although several metals have been incorporated into detergents, only two metal cations are now commonly used – calcium and magnesium. Heavy metals such as barium are no longer used.

The detergent can be neutral, where the salts are simple and contain roughly stoichiometric amounts of the metal and polar substrate. It is possible, however, to incorporate large amounts of metal base (for example calcium carbonate) by blowing carbon dioxide through a reaction mixture containing excess metal oxide or metal hydroxide, producing an overbased detergent , a typical example is shown below (Figure 8).

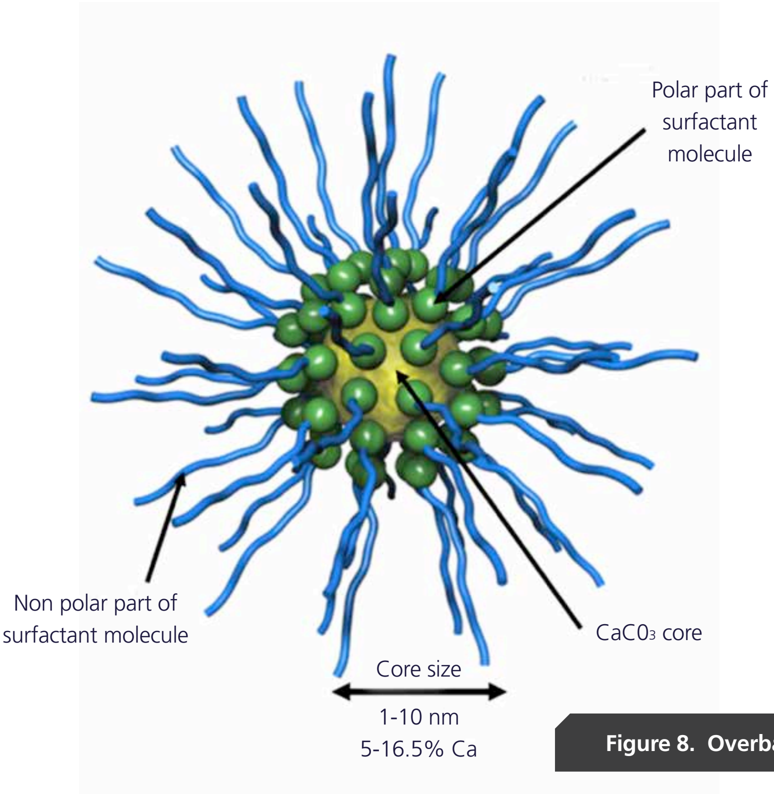


Figure 8. Overbased Detergent

The overbasing level is indicated by the Base Number (BN), measured using potentiometric titration (e.g. ASTM D-2896) which expresses the basicity of the detergent in terms of the equivalent number of milligrams of potassium hydroxide per gram of detergent.

Detergents reduce deposits and provide anticorrosion and antirust protection. Deposit precursors, being oil insoluble, have a greater affinity for detergent molecules than oil molecules. They are attracted to detergent micelles and trapped within them. Thus, they are kept in solution in the oil and cannot settle out to form deposits in the engine. On particles of less than 20nm diameter, the detergents form adsorbed films surrounding the particle surface, which slow down coagulation. Larger particles (50 – 150nm) usually have an electrically charged surface which can attract the detergent substrate which forms a stabilising layer thus preventing particle agglomeration.

Overbased detergents can also provide the large amount of base required to neutralise acidic components produced by fuel combustion (mineral acids) and by oxidation of the oil (organic acids). This reduces corrosive wear of the surfaces of iron (antirust protection) and other metals (anticorrosion) in the engine. Some detergent species can also function as antioxidants.

Dispersants

Dispersants consist of a polar head, the polarity of which is derived from oxygen or nitrogen moieties, and a hydrocarbon or oleophilic tail, typically poly isobutene, which enables the substrate to be fully oil soluble. They are generally referred to as ashless, containing no metal to form ash on combustion, but can also contain small amounts of boron derived from boric acid which is sometimes used as a capping agent.

Three main types of ashless dispersant are in use.

Succinimides

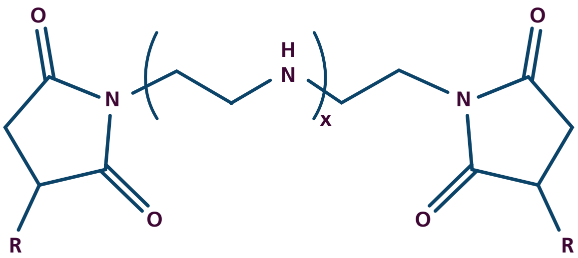


Figure 9. General Structure of a Succinimide Based Dispersant

Succinic esters of polyols

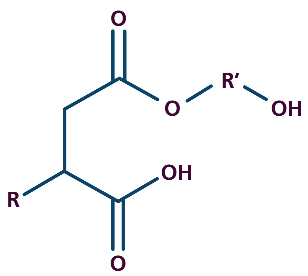


Figure 10. General Structure of a Succinic Ester of Polyols

Mannich bases

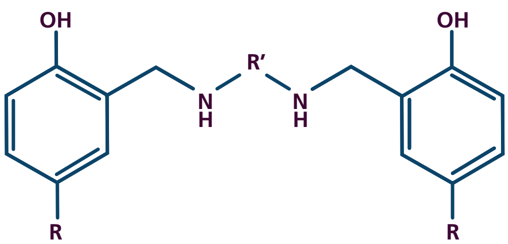
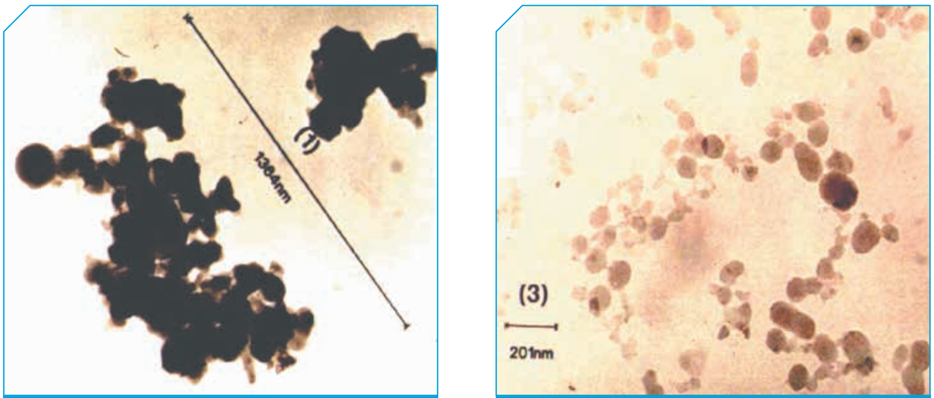


Figure 11. General Structure of a Mannich Base

Ashless dispersants have longer hydrocarbon tails than the detergents but function similarly in that they form micelles which trap deposit precursors such as soot or sludge. Particles up to about 50nm (cf. 20nm for detergents) can be stabilised by the thicker adsorbed film. Dispersants which contain an ionisable polar head (for example succinimides) can also stabilise larger particles by charge repulsion. An ashless dispersant micelle can attract and hold at least ten times more sludge particles than a detergent micelle. Their effectiveness is shown in Figure 12. Ashless dispersants are also highly effective at stabilising soot produced by diesel engines, preventing particle agglomeration and hence oil thickening.

Dispersant viscosity modifiers are ashless too, but have a higher molecular weight. They form even thicker barrier films by attaching themselves to particles at several points and can stabilise particles up to about 100nm.



Poor Dispersancy

Good Dispersancy

Figure 12. Dispersion by Dispersants

Inhibitors

Inhibitors are used to prevent, minimise or reduce wear, oxidation, corrosion, rust, friction and foam.

The main chemical families are zinc dithiophosphates (ZDDPs), hindered phenols, aromatic amines, phosphorus compounds, polysiloxanes and sulfurised fatty acid derivatives.

ZDDP additives have dialkyl moieties and can be subdivided into primary alkyl and secondary alkyl ZDDPs. Pentan-l-ol and 3-methylbutan-2-ol are illustrative of the primary and secondary alcohols used to prepare primary and secondary ZDDPS.

Different ZDDP chemical types perform differently (Table 4). Each type has important applications in modern additive packages. The choice of the alcohols used in the preparation of the ZDDP determines the relative effectiveness of the ZDDP as an anti-wear agent but also its ability to withstand the effects of heat and water i.e. thermal and hydrolytic stability.

Table 4. Performance Parameters of Different ZDDP Types

	Primary Alkyl	Secondary Alkyl	Aryl
Thermal Stability	Medium	Low	High
Antiwear Protection	Medium	High	Medium
Hydrolytic Stability	Medium	High	Medium

The general structure of a ZDDP is shown in Figure 13.

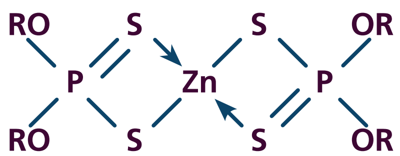


Figure 13. Zinc Dialkyl Dithiophosphates

Hindered phenols (Figure 14) function as antioxidants. Typically these are alkylated in the ortho position with bulky alkyl groups to form sterically hindered phenols such as 2,6-ditertiarybutyl paracresol.

Dialkylphenylamines (Figure 15) are representative of the chemical family of aromatic amine antioxidants.

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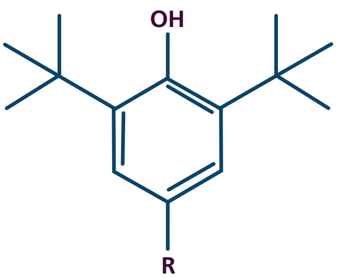


Figure 14. Hindered Phenol

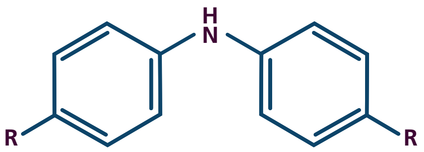


Figure 15. Diphenylamine

Figure 16 shows representative phosphorus compounds used as inhibitors.

dialkylhydrogen phosphite   trialkylphosphate

Figure 16. Phosphorus Based Inhibitors

Antiwear

Hydrodynamic lubrication is maintained by a multimolecular film of lubricant between the surfaces involved. If surfaces don't touch, there is no wear. However, hydrodynamic lubrication is not always possible. When loads are high, or the lubricant viscosity is too low, surface asperities on the moving parts make contact (Figure 17). This metal to metal contact between the lubricated surfaces is termed boundary lubrication. Under these conditions, reduction in friction is achieved through the adhesion of the antiwear additive to the metal surface and the formation of a lubricating solid film.

Most anti-wear agents work by forming low shear films on metal surfaces. ZDDPs are by far the most effective multifunctional types.

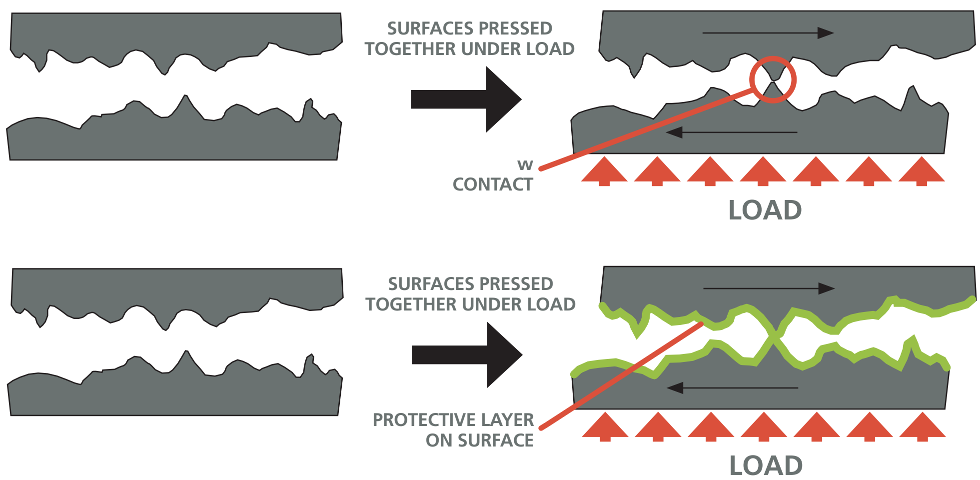


Figure 17. Illustration of Boundary Lubrication

The mode of action of phosphorus additives is similar to that of ZDDP. Their function is based on the reduction of friction during boundary lubrication through the adhesion of the additive or its thermal decomposition product to the metal surface layers.

Antioxidancy and Anticorrosion

Oxidation of an oil leads to the oil darkening and thickening as chemical species are broken down forming insoluble sludge or soot particles. Organic acids are produced which are extremely corrosive towards non-ferrous metals leading, for example, to bearing corrosion. Further oxidation leads to the build up of polymeric material. These high molecular weight oxygenated polymers cause oil thickening as well as varnish and gum deposits on pistons and other engine components.

Inhibitors work as antioxidants by disrupting the chain propagating steps of the oxidative process by which these insoluble species are formed (Figure 18). The oxidative process is a chain reaction which once started, propagates at an exponential rate producing increasing amounts of free radical and or peroxide species. The inhibitors themselves function as either peroxide decomposers or as free radical traps.

ZDDPs are able to act as antioxidants by disrupting the chain propagation steps of the oxidative reaction, by acting as either peroxide decomposers or free radical traps.

ZDDPs also act as metal deactivators or anticorrosion agents by forming protective films on metal surfaces.

Initiation:	**RH**	→	$R^{\bullet}$
Propagation:	$R^{\bullet} + O_2$	→	$ROO^{\bullet}$
	$ROO^{\bullet} + RH$	→	$ROOH + R^{\bullet}$
	ROOH	→	$RO^{\bullet} + HO^{\bullet}$
	$RO^{\bullet} + RH$	→	$ROH + R^{\bullet}$
	$HO^{\bullet} + RH$	→	$R^{\bullet} + H_20$
Termination:	$R^{\bullet} + ROO^{\bullet}$	→	**ROOR**
	$R^{\bullet} + R^{\bullet}$	→	**R-R**

Figure 18. Oxidation Chain Reaction

Hindered alkyl phenols intercept deleterious free radicals to form stable hindered radicals which are not prone to propagation (Figure 19). These free radical traps help maintain the viscosity characteristics and long term performance of the lubricant, limiting damage to the viscosity modifiers, and reducing lacquer formation from the base oil.

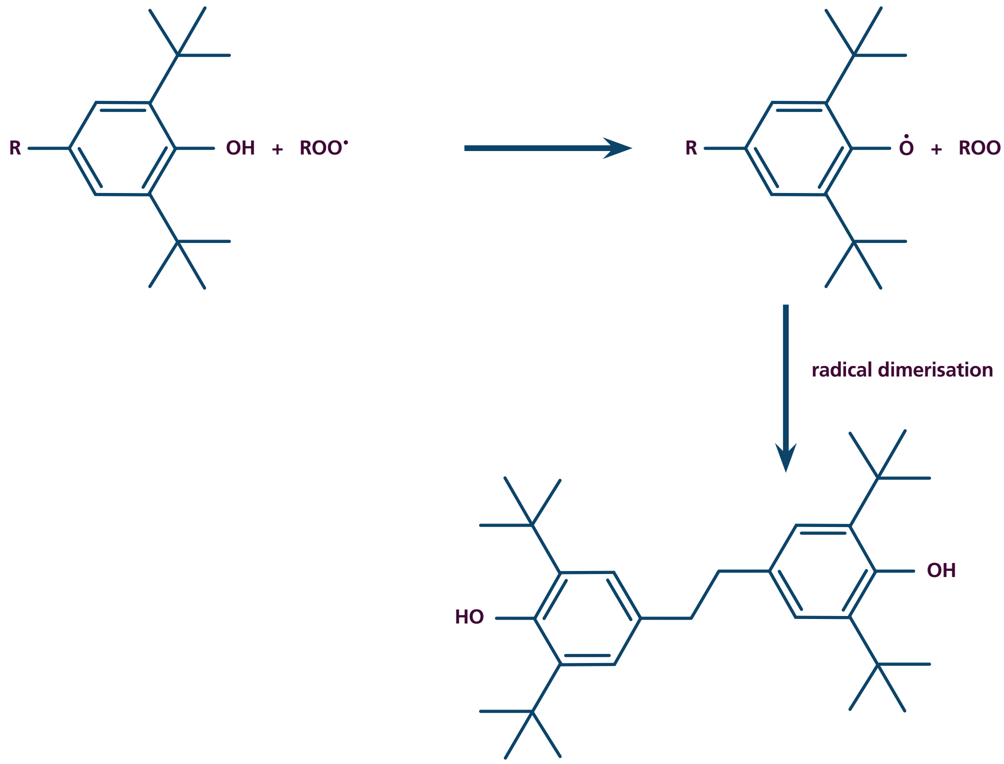


Figure 19. Radical Trapping by Hindered Phenols

Aromatic amines act synergistically to the phenolic family[16].

Antifoam Agents

The presence of additives can slow up the release of gases churned into lubricating oil. This may result in foaming and/or air entrainment. Air entrainment, especially in modern, high speed, high temperature engines, may result in diminished engine reliability.

Foam is countered by adding tiny amounts of antifoam additives. Silicon chemicals, such as polydimethylsiloxanes (20) are very commonly used as antifoam agents.

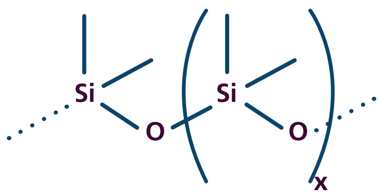


Figure 20. Polymethylsiloxane Antifoam

Since these materials are not very oil soluble, they separate from the oil onto the surface of air bubbles and cause them to rupture by reducing the surface tension. Common treating dosages for such antifoams are between 10 to 100 ppm in oil.

Polyacrylates are particularly effective air release agents.

Friction Modifiers

Power loss from friction in internal combustion engines is derived from the viscous drag of the lubricant and friction losses through heat generation under mixed and boundary lubrication conditions. The former can be reduced by decreasing the viscosity of the oil, but only to the point where a lubricant film is maintained, which keeps moving parts separated.

Boundary lubrication occurs in various stressed parts of the engine, for example between rings and liners at the top of the piston travel and in the valve train between cam and lifters. In this type of lubrication the oil film is not adequate to keep moving parts separated and this function is taken over by a film of polar molecules strongly absorbed on the metal surface. The drag caused by this boundary lubrication depends on how easily these surfaces slide past one another. One way to reduce the energy losses and maintain a boundary film is by using friction modifiers.

By definition, the base fluid itself is the primary friction modifier, but the need for fuel economy has required additional friction modifiers. Friction modifiers are closely related to antiwear additives in mode of action. They are generally straight hydrocarbon chains with a polar head group. Typical polar head groups are:

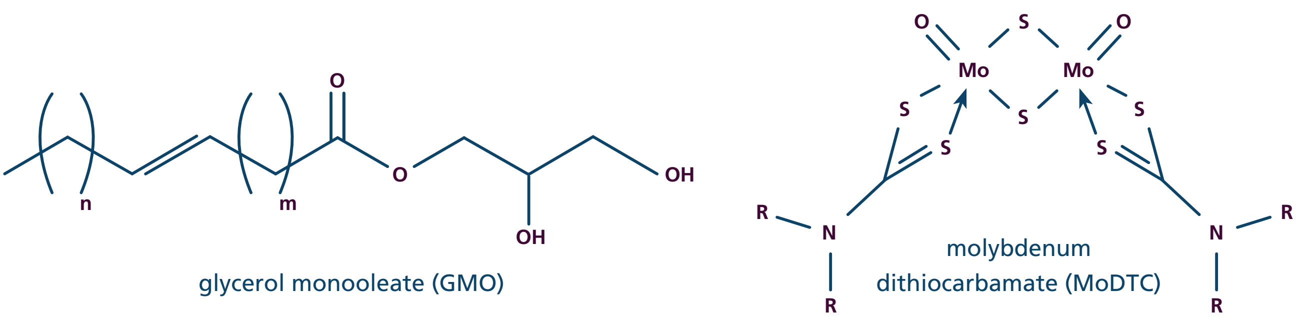
- Amines, amides and their derivatives
- Carboxylic acids or derivatives
- Phosphoric or phosphonic acids and their derivatives

The polar head groups are attracted to the metal surface and form relatively strong bonds whilst the long hydrocarbon tail is left solubilised in the 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.

Molybdenum compounds such as molybdenum dithiocarbamates, molybdenum dithiophosphates and other more complex molybdenum compounds are extensively used for friction modification. These compounds react on the metal surface to yield molybdenum disulfide which has a structure that allows sliding and shearing to take place.

Examples of common friction modifier types are listed below. Their treating dosages range from 0.1 to 1.5% and chemical types include:

- Sulfurised fats and esters
- Amides of fatty acids
- Polyol esters of fatty acids e.g. glyceryl monooleate (GMO, Figure 21)
- Molybdenum compounds e.g. molybdenum dithiocarbamate (MoDTC, Figure 21)



glycerol monooleate (GMO)

molybdenum dithiocarbamate (MoDTC)

Figure 21. Friction Modifiers

Pour Point Depressants

These additives act to lower the pour point of an oil which is the lowest temperature at which an oil will pour or flow when cooled. A low pour point is particularly important for proper performance of lubricants in cold climates.

The most common chemical types are polyalkylacrylates and the polyalkylmethacrylates (Figure 22), also often known as polyacrylates and polymethacrylates.

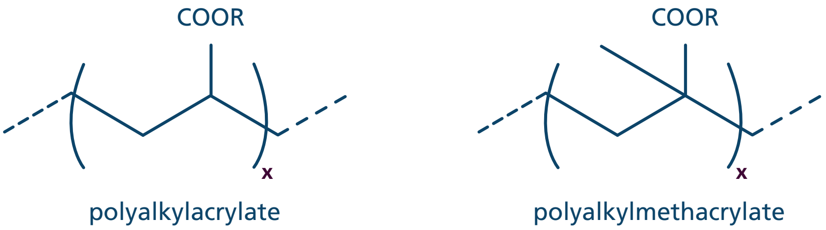


Figure 22. Pour Point Depressants

At low temperatures, the wax left in the lubricant base stock comes out of solution as wax crystals, producing a gel-like structure which impedes the flow of lubricant to critical engine parts. Pour point depressants are added, not to reduce the amount of wax, but to inhibit the formation of interlocking crystal networks.

Common treat rates range from 0.1 to 0.5 % mass in the finished lubricants.

Viscosity Modifiers

By suitable formulation, it is possible to make an engine lubricant which satisfies both the low and high temperature requirements of the SAE Viscosity Classification System, J300. High molecular weight polymers, known as viscosity modifiers or viscosity index improvers are commonly used for this purpose. Such oils are referred to as multigrade oils (e.g. SAE 10W40). Their viscosity is less sensitive to temperature than that of monograde oils having the same high temperature viscosity (e.g. SAE 40). As a consequence, multigrade oils allow acceptable engine operation over a much wider temperature range. These effects are shown schematically in Figure 23.

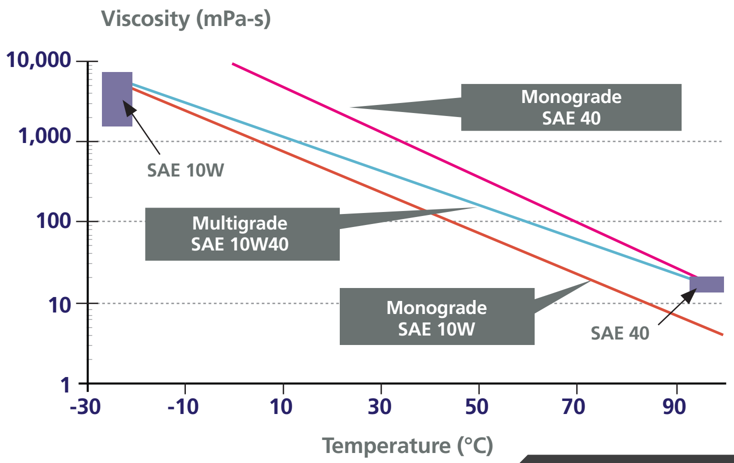


Figure 23. Effects of Temperature on Viscosity

Multigrade oils have a lower viscosity at low temperatures allowing easier engine cranking and starting than the corresponding monograde oil and as a result improved fuel consumption. Viscosity modifiers have also been shown to a vital role to play in improving the durability of fluids by improving the load bearing capacity when compared to a monograde oil[17].

Higher molecular weight polymers (from 50,000 to 500,000 Da) of various chemical types are used as viscosity modifiers for multigrade lubricants. The main chemical families are olefin copolymers, hydrogenated styrene-diene copolymers (Figure 24) and polyalkylmethacrylates.

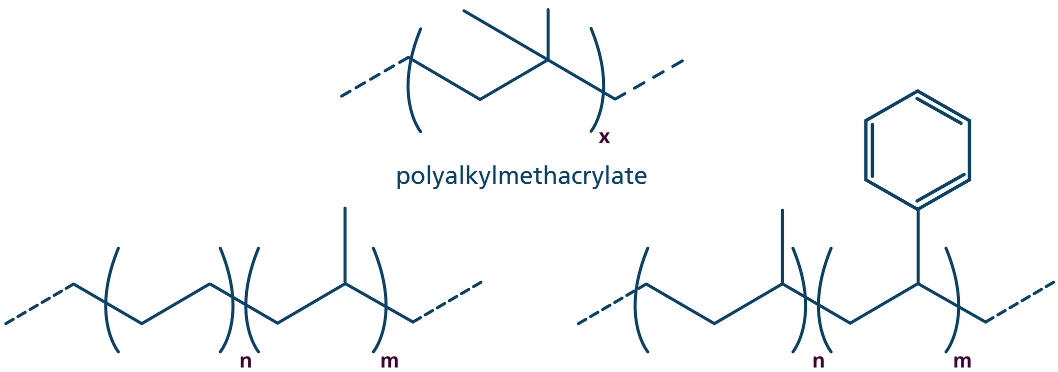


Figure 24. Viscosity Modifiers

For ease of application, viscosity modifiers are generally diluted in a low viscosity base oil to a concentration of between 5 and 15 % mass depending on the solubility and the viscosity of the polymer. The function of the viscosity modifiers is to decrease the slope of the viscosity /temperature relationship (cf. Figure 21).

In addition to their ability to modify oil viscosity, viscosity modifiers can provide other functions. This includes load bearing capacity mentioned previously and also dispersancy. This goal is generally achieved by copolymerisation of specific polar monomers (such as those delivering amine basicity) with the primary monomers of the alkyl methacrylate or hydrocarbon types.

Dispersant viscosity modifiers are often used to supplement ashless dispersants and sometimes allow reduction in ashless dispersant level. Dispersant viscosity modifiers can exhibit good gasoline sludge control and excellent diesel soot handling. Some dispersant viscosity modifiers also exhibit improved wear control due to a reduction in abrasive wear.

Components and Performance Packages

Finished engine lubricants contain a number of individual additive components – typically about eight but ranging from five to fifteen. Some or all may be blended individually into the lubricant basestock during manufacture. More typically, the components are pre-blended by the additive manufacturer into a performance additive package which is sold to the lubricant marketer. The viscosity modifier, which is a major component of multigrade engine lubricants, is usually purchased and blended separately by the lubricant marketer. Figure 25 illustrates this schematically.

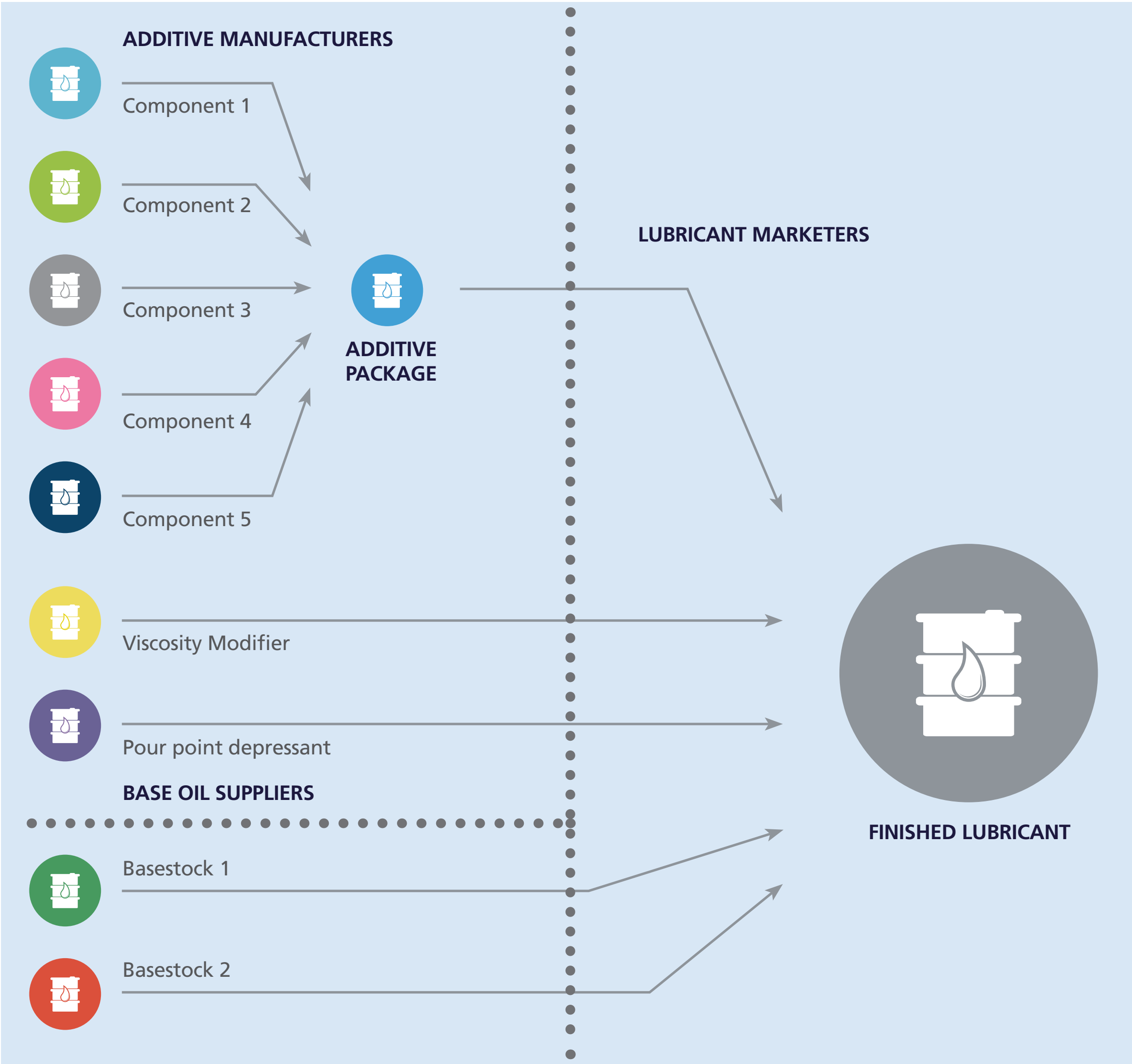


Figure 25. Component and Package Formulation

A performance package is therefore a complex mixture of several components blended carefully together. Formulating a performance package is technically challenging and costly, requiring considerable expertise and expensive performance testing. The different components can have synergistic or antagonistic effects on a given performance parameter due to chemical interactions or competition at the metal surface. They can also exhibit physical or chemical incompatibility unless balanced correctly.

Typical finished lubricant compositions, based on weighted averages, have been established for PCMO and HDEO categories. The lubricants are first split into their main component categories - base oil, viscosity modifier, and performance package, see Figure 26. The performance package is then further split into its major constituent additive components, see Table 5 and Figure 27.

Table 5. Weighted-Average Engine Lubricant Composition, Mass Percent

Additive component	Passenger Car Motor Oil	Heavy Duty Diesel Oil
Ashless dispersant	6.5%	6.6%
Metal detergent	2.5%	3.3%
ZDDP	1.1%	1.2%
Inhibitor	1.4%	0.8%
Total Additive Content	11.5%	11.9%
Viscosity modifier	10.9%	10.0%
Base stock	77.6%	78.1%
Total	100.0%	100.0%

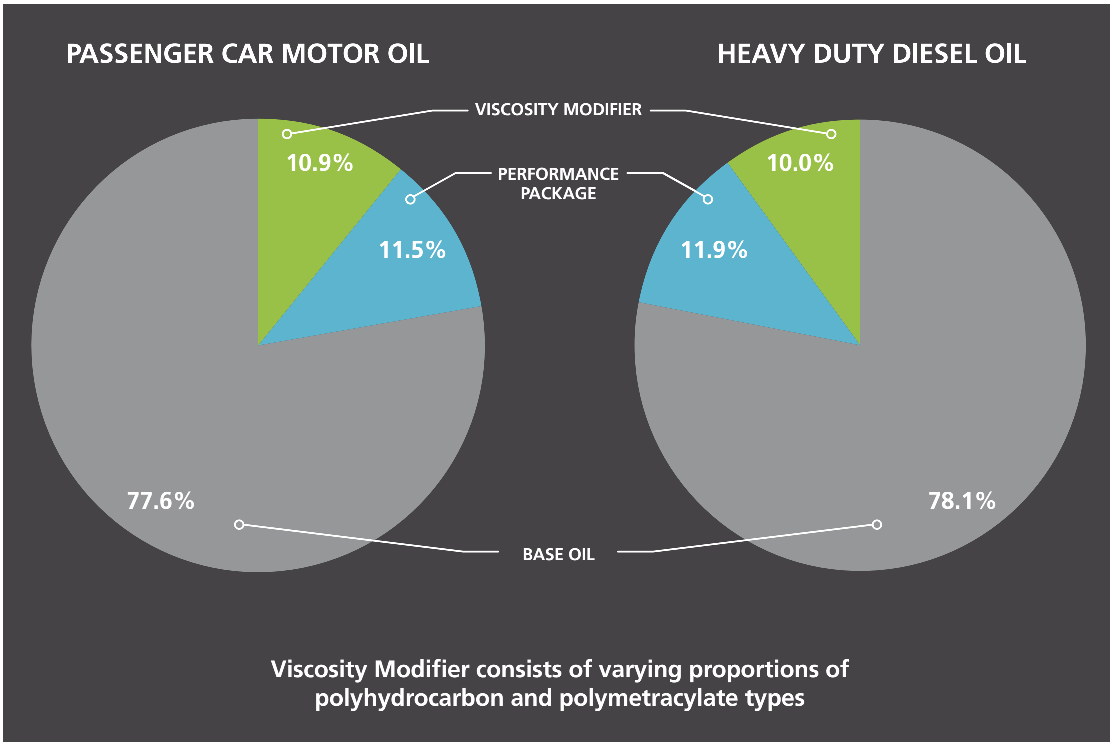


Figure 26. Finished Engine Lubricant Formulations

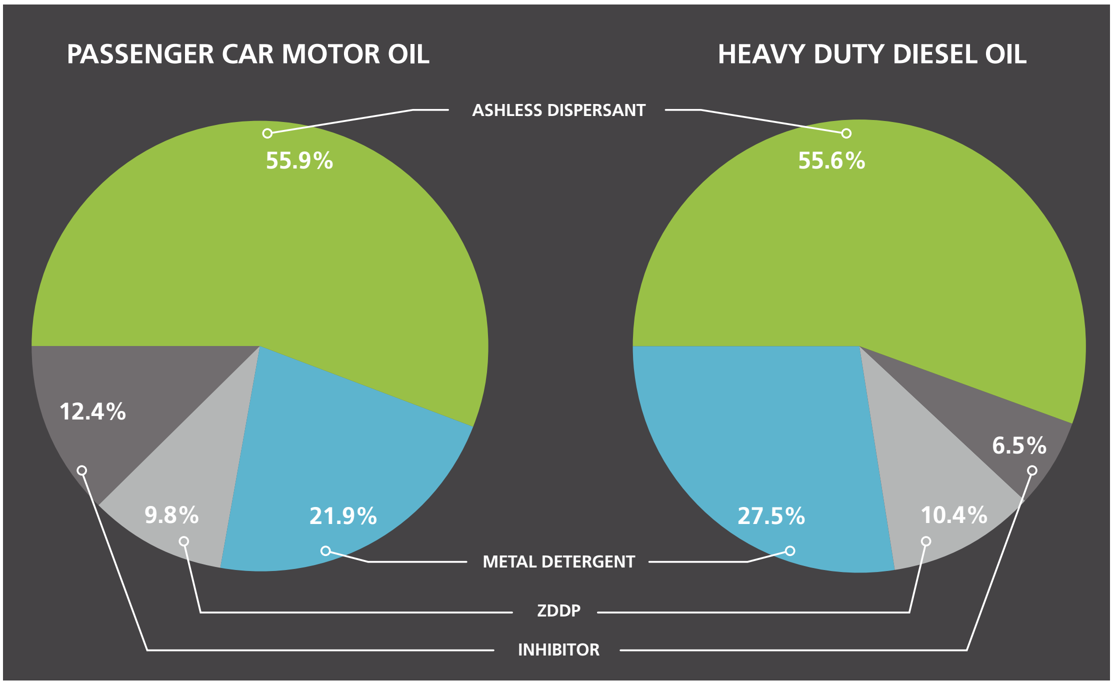


Figure 27. Performance Package Formulations

Typical Performance Additive Packages

Hundreds of different additive packages are on the market - all confidential to the supplier. The average composition of a typical performance additive package is based on data from commercially available formulations provided by the main additive suppliers. The following additive categories were used: ashless dispersants, metal-containing detergents and zinc dialkyldithiophosphates. Small volume specialised components, such as anti-oxidants, friction modifiers, supplemental AW - are included with the inhibitors. Simple calculations using the total engine oil tonnages in Table 2 and the formulations in Figure 26 and 27 give us tonnages for these principal additive components (Table 6).

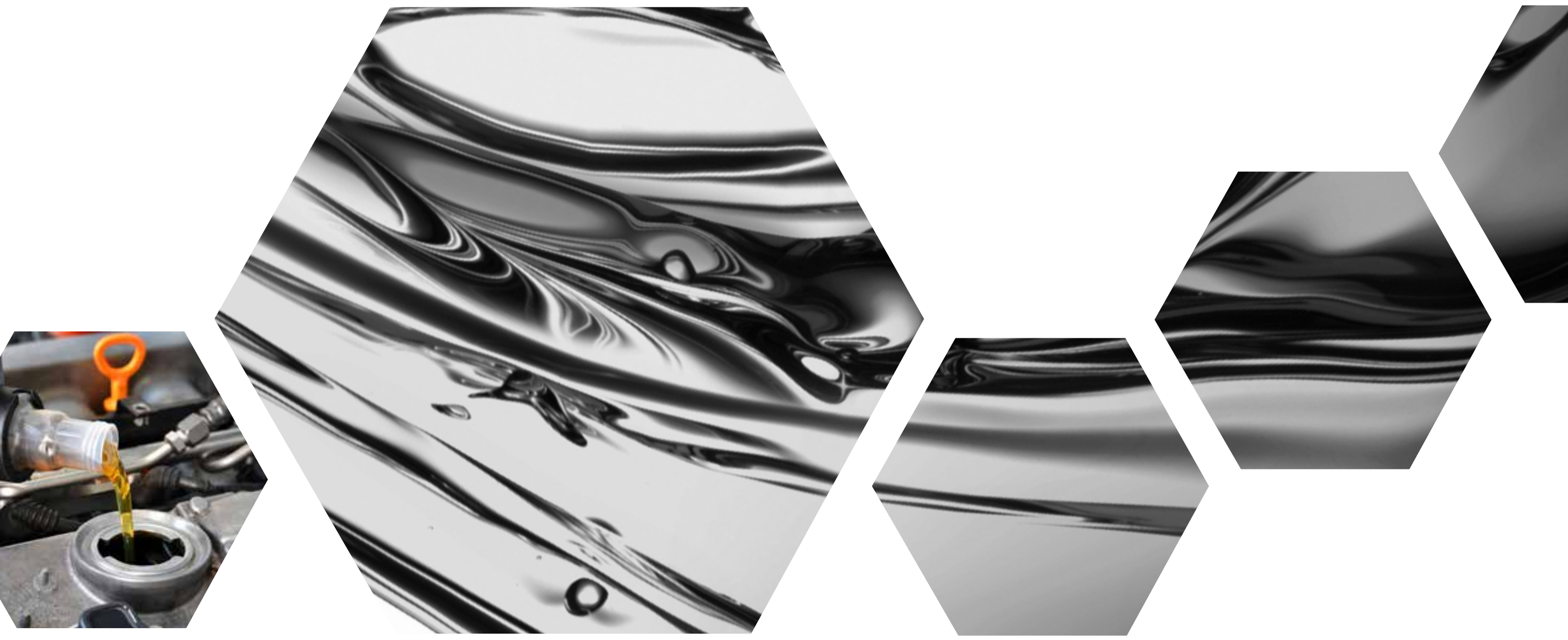


Table 6. Market for Engine Oil Additive Components in 2007 and 2015

Market for engine oil additive components Calculated from weighted average typical lubricant composition Europe (kilotonnes)						
	2007 - EU 15			2015 - EU 28		
Additive component	PCMO	HDDO	Total	PCMO	HDDO	Total
Performance Package						
Ashless dispersant	64.7	72.4	137.1	89.0	68.7	157.7
Metal detergent	32.1	42.0	74.1	34.8	34.0	68.8
ZDDP	13.2	15.8	29.0	15.6	12.9	28.5
Inhibitor	10.1	8.8	18.9	19.8	8.0	27.8
Sub-Total Performance Package	**120.2**	**139.0**	**259.1**	**159.2**	**123.6**	**282.8**
Viscosity Modifiers						
VM	70.8	95.5	166.3	147.4	102.3	249.7
D-VM	2.6	1.9	4.5	1.6	1.6	3.2
Sub-Total Viscosity Modifiers	73.4	97.4	170.8	149.0	103.9	252.9
Total	**193.6**	**236.4**	**430.0**	**308.2**	**227.5**	**535.7**

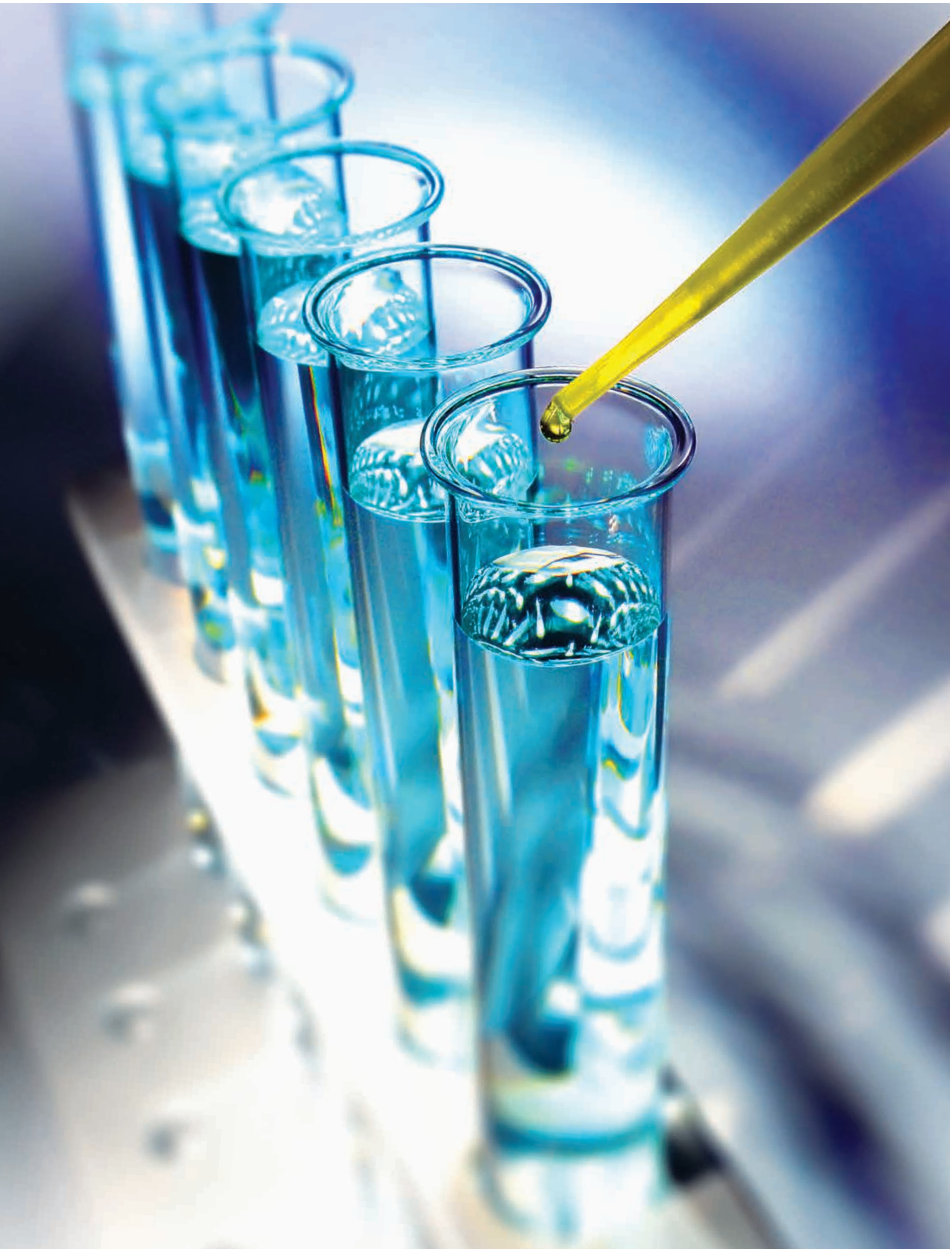
Comparing the 2015 data in Table 6 to the 2007 data shows some interesting trends such as the continuous decrease in metal detergents – visible in both passenger car and heavy duty vehicle lubricants – reflecting a larger market penetration of low sulfated ash formulations. Also a decline in ZDDP levels is seen which is driven by the concerns about the impact of Phosphorus and Zinc on exhaust gas after-treatment systems. A sharp increase of inhibitor concentrations is seen in recent years which can be attributed to higher requirements on oxidation stability and fuel economy performance of modern engine oils.

Viscosity Modifiers

The different types of viscosity modifiers (i.e. olefin copolymers, hydrogenated styrene-diene copolymers and polyalkylmethacrylates) have been combined for this study. Occasionally they are mixed with the additive package, but are more usually sold separately, and blended by the lubricant producer according to the finished oil formulation.

If we look at the overall lubricant composition it becomes apparent that the average treat rate (Figure 26) as well as absolute volume (Table 6) of viscosity modifiers have increased, in particular for the passenger car vehicle segment. This is a reflection of increased performance requirements on viscosity control during extended drain intervals: enabling longer drain requires more high performance additives.

Nowadays, most engine lubricants are multigrade, containing viscosity modifiers. However, some monograde oils are still sold in Europe, but as the volume is small monograde oils have not been taken into account when estimating weighted average typical viscosity modifier concentrations.



Health, Safety and the Environment

Health, Safety and the Environment

Introduction

Lubricant additive packages are multi-component blends sold to industrial customers. The risk of exposure of these products to man and the environment is already tightly controlled by existing EU legislation concerning protection of workers, emissions to air, water and soil, and disposal of waste.

In addition to legislative drivers, the lubricant additives industry, represented in Europe by the ATC, has an ongoing commitment to provide accurate and up-to-date health, safety and environmental advice to all downstream users. In particular, the ATC has taken an active and informed role in communications on Health, Safety and Environmental matters, such as developing generic exposure scenarios for lubricant mixture in order to comply with REACH, disclosure of appropriate detail on composition and hazard information and producing best practice guidelines for specific substances.

Historically, additive manufacturers have collaborated in the testing of major additive classes to generate data on a significant number of chemical classes, covering the main additive families included in engine lubricants. A recent example of this was the Consortia or Substance Information Exchange (SIEF) activity for registration of 2010 and 2013 substances under REACH as well as the voluntary participation in national and international chemical initiatives (e.g. US EPA High Product Volume; ICCA SIDS).

REACH

The majority of lubricant additives are of low mammalian toxicity[4]. Some lubricant additives are harmful to aquatic organisms and most show a degree of persistence. However these additives are typically of low water solubility and when handled and disposed of according to manufacturers' recommendations are considered not to present a significant environmental risk[18]. Additive suppliers provide this information to downstream users through hazard communication documents such as the Safety Data Sheet (SDS), exposure scenarios annexed to the SDS where required by REACH and the product label, which contain relevant instructions for safe storage, use and disposal.

Under the REACH regulation, companies are responsible for providing information on the hazards, risks and safe use of chemical substances that are manufactured in or imported to the EU[19]. ATC has been a key enabler for lubricant additive companies to meet their obligations under REACH; providing a forum for data sharing through the ATC REACH consortium enabling the registration of relevant substances in accordance with the regulatory timetable, developing Specific Environmental Release Categories[20] which reflect actual conditions of use for lubricant applications and along with our partners in the lubricant supply chain, ATIEL, developed simplified guidance covering identified use communication in the supply chain[21].

ATC have worked together with ATIEL to develop a process for supporting the communication of safe use of our products under REACH. This work, coordinated by the ATIEL / ATC REACH Working Group, includes the identification of use information and development of generic exposure scenarios (GES) for common lubricant end uses[22].

The objective of the GES is to offer everyone in the lubricant supply chain a standardised format for their exposure scenarios and common language and terminology to use in those documents.

ATC activities have enabled compliance with the REACH regulation for our members, enhanced communication throughout the lubricant supply chain and developed a process for supporting the safe use of our member's products under REACH.

Additive Improvements

Stricter regulations on Health, Safety, and the Environment (HSE) are a main driver to improve and develop new additive components. Some additives have been classified to a higher risk category as irritant or toxic materials, and concerns have been raised about the use in customer products. Additive companies and lubricant suppliers have responded to these concerns by developing new additives which do have less impact on the environment. Some substances are not used anymore in modern engine oils. For example, additives containing Chlorine or Barium were used for specific performance properties but their use has been abandoned due to their toxicity. The elemental content of a typical engine oil is shown in Table 7 (average of data supplied by main additive suppliers).

Table 7. Elemental Content of Engine Oils

Elements from additives - weighted averages (mass %)		
	Passenger Car Motor Oil	Heavy Duty Diesel Oil
Calcium & magnesium	0.18%	0.22%
Nitrogen	0.08%	0.06%
Zinc	0.08%	0.08%
Phosphorus	0.07%	0.08%
Sulfur	0.19%	0.23%
Plus other contributions to carbon, oxygen and hydrogen contents		

Reducing the amount of sulfur being released to the environment has received increased attention, leading to low sulfur fuels in the European market. Sulfur is an important ingredient in engine oil being present in detergents and in the antioxidant/antiwear agent. During the operation of an engine a small amount of engine oil can enter the combustion chamber (in the form of an oil mist or by blow-by at the piston rings) where it is burned and released to the environment. Stricter limits on the sulfur content in engine oil have been introduced in ACEA C and E categories which are classified as Low SAPS ("Sulfated Ash, Phosphorous and Sulfur) oils. Part of this reduction is achieved by lesser use of Group I base oils in modern engine oils. Higher quality base oils are virtually sulfur-free due to enhanced refining steps. However, if the concentration of protective sulfur-containing additives is reduced, engines will be more susceptible to wear and corrosive attack by organic acids. Alternative components will need to replace the functionality that sulfur containing components currently provide.

The need for reduced sulfur content in oils has led to a more widespread use of sulfur free detergents such as salicylates (see Chapter "Chemistry of Lubricant Additives"). The polar head of this detergent class contains a carboxylic acid group which does not contain sulfur. Being surface active it provides detergency power to keep metal engine parts clean from deposits.

Zinc present in engine oils is derived from ZDDP (zinc dialkyl dithiophosphate) which is added to provide wear resistance, in addition to antioxidant properties as ZDDP inhibits the branching step by removing hydroperoxides from the oil. Several ZDDP replacement additives have been developed over the years as alternative anti wear agents. Although hardware developments enable the reduction of ZDDP in modern Low SAPS engine oils it is still a widely used ingredient due to its unique combined properties. To maintain sufficient oxidation resistance generally higher amounts of supplementary antioxidants are used.

Molybdenum dithiocarbamate (MoDTC) (see chemistry section) is widely used in engine oils to achieve a reduction in engine friction for improving fuel economy. Together with zinc dialkyldithiophosphates (ZDDPs) antiwear additives, MoDTC gives a friction reduction in the boundary lubrication regime by formation of a tribochemical reaction film (so-called tribofilm). This tribofilm formation, however, does depend on the surface properties. Modern engine parts can utilise alternative coatings (such as diamond-like carbon (DLC)) which provide a smooth, inert surface to reduce engine friction. These inert surfaces can prevent traditional anti wear agents forming a tribofilm, this has led to the application of metal-free friction modifiers. Further insights in the tribological behaviour have led to the development of novel organic friction modifiers to achieve improved friction properties as compared to conventional organic friction modifiers, such as glycerol mono-oleate and oleylamide.

As engine oils are becoming lower and lower in viscosity, new components and additive formulations may be required to maintain engine durability.

Exhaust Emissions

Vehicle and engine system designs have to meet increasingly stringent exhaust emission standards, as exemplified by the data provided in Table 8 covering Global emission standards for Heavy Duty vehicles over time[23]. Similar trends in terms of a reduction in emissions have also applied to passenger car vehicles, with the latest Euro VI requirements for passenger car vehicles having 90% lower emission requirements than the first standards which were introduced in 1992. Higher performance lubricant additives are required to cope with the more severe engine operating conditions in the low emissions designs being developed by OEMs. Vehicle maintenance is a key aspect of long term emissions control. US EPA and UK RAC tests both report that approximately 15% of the passenger car population in the USA and UK causes approximately 55% of passenger car related air pollution[24]. Original equipment manufacturers are focusing on higher performance lubricants, more robust vehicle system designs, and on-board diagnostic systems (OBD) to achieve their targets of long term integrity of emissions systems.

Table 8. Global Emissions Standards for Heavy Duty Vehicles

Stage	Date	CO	HC	NOx	PM	PN	Smoke
		g/kWh	g/kWh	g/kWh	g/kWh	1/kWh	1/m
Euro I	1992, ≤ 85 kW	4.5	1.1	8	0.612		
	1992, > 85 kW	4.5	1.1	8	0.36		
Euro II	1996.1	4	1.1	7	0.25		
	1998.1	4	1.1	7	0.15		
Euro III	1999.10 EEV only	1.5	0.25	2	0.02		0.15
	2000.1	2.1	0.66	5	0.10a		0.8
Euro IV	2005.1	1.5	0.46	3.5	0.02		0.5
Euro V	2008.1	1.5	0.46	2	0.02		0.5
Euro VI	2013.01	1.5	0.13	0.4	0.01	8.0×10^{11}	

a - PM = 0.13 g/kWh for engines <0.75 dm3 swept volume per cylinder and a rated power speed > 3000 min-1

Emission Reduction

Emission reduction in Europe has made impressive progress over the last decades. Since the introduction of defined emission limits from EURO I(1) to Euro VI(6), heavy and medium duty engine designers have adapted to these regulations. Significant effort has been made by the OEMs to achieve these standards via combustion optimisation and aftertreatment systems.

Figure 28 shows the cumulative amount of NOx and PM emissions from 1990 to 2020 of heavy duty commercial vehicles in Germany. It is a visual representation of the progress made in this area. This indicates how the different emissions standards have affected either PM and/or NOx as the car fleet has evolved. For example, the introduction of Euro II(2) significantly reduced PM but did not affect NOx. As the Euro I(1) vehicles are removed from the car fleet, the total emission levels reduce substantially. Euro VI(6) vehicles have a very small contribution to the total due to their advanced emission reduction technology.

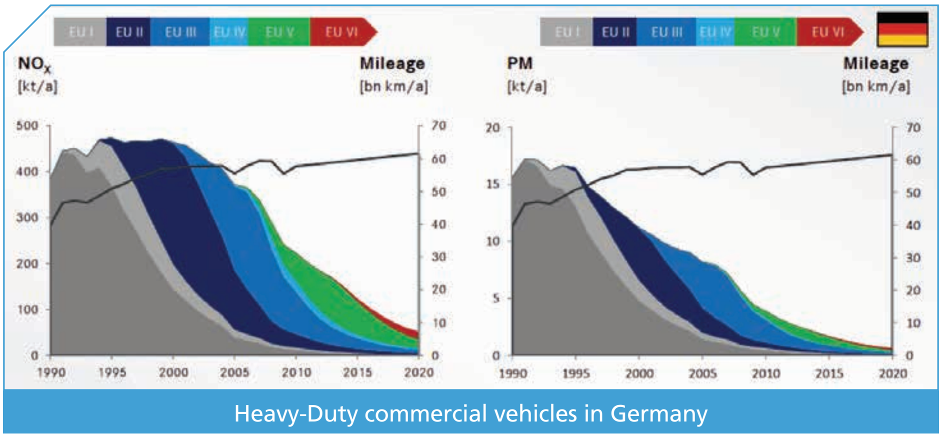


Figure 28: Cumulative Emissions of NOx and PM from Euro I to Euro VI

The emissions reduction achievements by OEMs are even more impressive when the overall increase in mileage is considered. The emissions have reduced substantially, even though there has been around 30% increase in total mileage over this time period. This underlines the success of exhaust emissions reduction and the overall positive impact on our environment.

It can also be noted that with the introduction of a new emissions standard, the contribution from the previous technology has reduced relatively quickly. Governments have encouraged and accelerated the removal of older technology from the marketplace. This has to be balanced with an increase in production costs due the more advanced technology required in newer vehicles. The transition to Euro VI is connected with a higher vehicle prices because of the necessary additional components in the aftertreatment system.

For Euro VI, all major heavy duty engine manufacturers in Europe added Diesel Particulate Filters (DPFs) to meet the legislated particle emission limits.

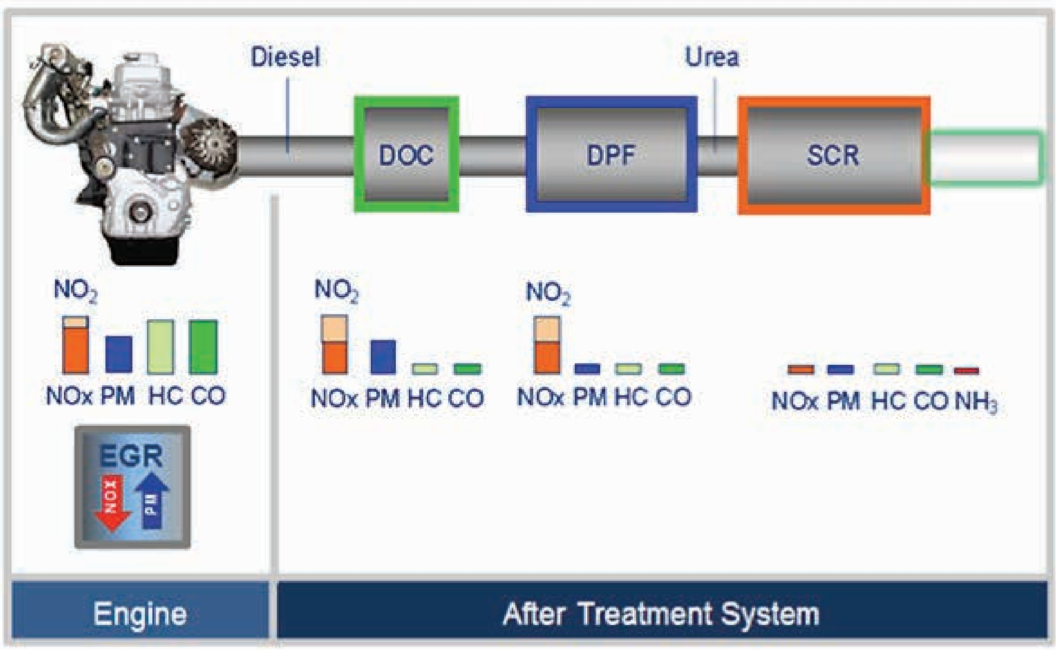


Figure 29 Emission Reduction in a Euro VI Heavy Duty Commercial Vehicle

Figure 29 shows a schematic diagram of typical Euro VI heavy duty commercial vehicle emission reduction equipment. A certain amount of exhaust gas is fed back to the engine right after combustion by the Exhaust Gas Recirculation (EGR) system. The components of the EGR are considered part of the engine package rather than the aftertreatment system. The share or the rate of circulated gas is related to engine calibration and can be optimised for different conditions. Typically this is a trade-off between increasing particle matter (PM) and reduction of nitrous oxide (NOx). Before Euro VI, manufacturers simply increased the levels of EGR to bring NOx down. However, this had the effect of increasing oil soot level at the same time.

The following components of the aftertreatment system are designed to reduce specific chemical species in the exhaust. After the diesel oxidation catalyst (DOC) reduces organic emissions, the Diesel Particulate Filter (DPF) is designed to reduce amount of particulate matter (PM) in the exhaust gas.

The Selective Catalytic Reduction (SCR) is the last component and is designed to minimise NOx to as low a level as possible. Different to all other systems, the SCR needs a reaction fluid that is called Diesel Exhaust Fluid (DEF) (alternatively known as AdBlue® or sometimes Urea). DEF is supplied by a separate tank that is located close to the fuel tank of the vehicle and is injected via a nozzle right before the catalyst. Other systems are in place to regenerate the rest of the aftertreatment system to maintain its performance. For example, injecting diesel is a common way to increase the temperature of the exhaust system to burn off contaminations in the DPF. By doing this, aftertreatment components last longer and service intervals can be extended. This can affect the requirements for the engine oil as higher amounts of fuel dilution are noted when regeneration is used. This is discussed in more detail in the Alternative Fuels section.

EGR, DPF and SCR components are strongly connected and their contribution to overall emission reduction can be balanced differently. The main vehicle manufactures in Europe have different approaches in their own hardware to achieve the same emissions target.

The aftertreatment systems described above mostly relate to diesel engines, however increasing use of Gasoline Direct Injection (GDI) in gasoline passenger cars means that they may also be challenged to reduce particle emissions. A solid particle number (PN) limit of 6.0×10^11 (equal to the limit already in place for diesel cars) will become effective for gasoline direct injection (GDI) vehicles from September 2017.

Passenger Car manufacturers have been developing methods to control PN emissions directly within the gasoline combustion process, such as advanced fuel injection strategies and/or the introduction of Gasoline Particulate Filters (GPF). Gasoline particulate Filters (GPF) utilise the same type of wall-flow substrates used in Diesel Particulate Filters (DPF). A GPF can be included in the exhaust system in addition to the three-way catalyst (TWC), or alternatively a TWC coating can be applied onto the GPF substrate.

Protection and compatibility with these aftertreatment systems are key drivers for the development of advanced automotive lubricant additives. New additives have been required to guarantee the lifetime of aftertreatment systems.

This is due to the accumulation of ash in particulate filters causing pressure increase in the aftertreatment system. This can lead to fuel consumption increase and reduced power output. Some chemicals traditionally found in automotive lubricants (including phosphorus and sulfur) have been linked to poisoning of catalyst surfaces. Hence many automotive lubricant specifications limit the levels of Sulfated Ash, Phosphorus and Sulfur that can be contained in the lubricant. This has led to the development of so called Low SAPS engine oils.

Table 7 shows the reduced level of these elements in modern engine oils compared to previous analyses. The represents the increasing presence of lower SAPS lubricants in the marketplace. The reduction of SAPS is a big challenge for formulators, completely new ways to maintain or even increase the engine oil performance are needed while constrained by tightening elemental limits.

Use of these Low SAPS oils has been a success and has shown to extend the interval for DPF cleaning procedures significantly without sacrificing the protection of the engine. Latest additive technology in Low SAPS oils have been shown to achieve at least as good durability protection than previous higher SAPS lubricants. These effects show the strong link between robust and lasting engine performance, emission reduction and high quality engine oils with the latest additive technology. This trend will continue as further emission reductions are demanded from the OEMs. For example the introduction of GPFs may introduce further changes in additive and oil formulation design for gasoline vehicles.

Engine Oil Consumption and Disposal

The composition of the engine lubricant changes during use. Some additives are chemically changed or even consumed as part of their functionality, and any contaminants of combustion generated during the course of engine operation which are not swept into the exhaust stream are neutralised and dispersed within the lubricant. It is widely accepted that used oil drained from the engine sump will contain polyaromatic hydrocarbons generated by the combustion process and this waste is suspected to pose a carcinogen risk through accidental skin contact. A significant number of motorists routinely perform engine oil changes themselves and so consumer product labelling and consumer education against inappropriate contact or disposal of used lubricants is part of an active safeguards programme within the oil marketing industry. This, together with a legal requirement to dispose of used oil at dedicated collection facilities serve to minimise the environmental and human risks from used oil.

Even though some proportion of waste oil is not recycled or reused, it is still vital that it is collected and disposed of correctly (usually via incineration) rather than released into the environment. Increasing legislation across Europe is designed to reduce the volume of oil that is improperly disposed of in the environment. The overall volume of waste oil is also reducing as sump sizes decrease, drain intervals increase and oil consumption reduces. This has partly been enabled by improvements in additive technology. For example, improved durability from the oil allows OEMs to downsize engine and increase drain interval.

The collection of used lubricants is becoming increasingly important and European legislation has evolved to encourage the collection of waste automotive lubricants. The collection and disposal was covered by the Waste Oil Directive[25] which required all waste oil to be collected. This also encouraged the reclamation and recycling of the waste oil. However, this was repealed on 12 December 2010 and waste oils are now governed by the Waste Framework Directive[26]. This states that waste oils should be collected separately and treated in accordance to the waste hierarchy. This also prioritises prevention, re-use, recycling, recovery and disposal as the last option. Member states are asked to ensure adequate waste oil collection legislation is in place to ensure this is adhered to.

A recent critical review[27] of the fate of waste oil shows that there is wide variation in unaccounted for waste oil by country see figure 30. Overall there is around 2400 kT of collectable waste oil produced in Europe, 70% of which is Engine Oil (the rest being industrial oils). In 2000 the average collection rate is 70 – 75% in the EU but there is a large variation by country with some achieving much higher rates of collection.

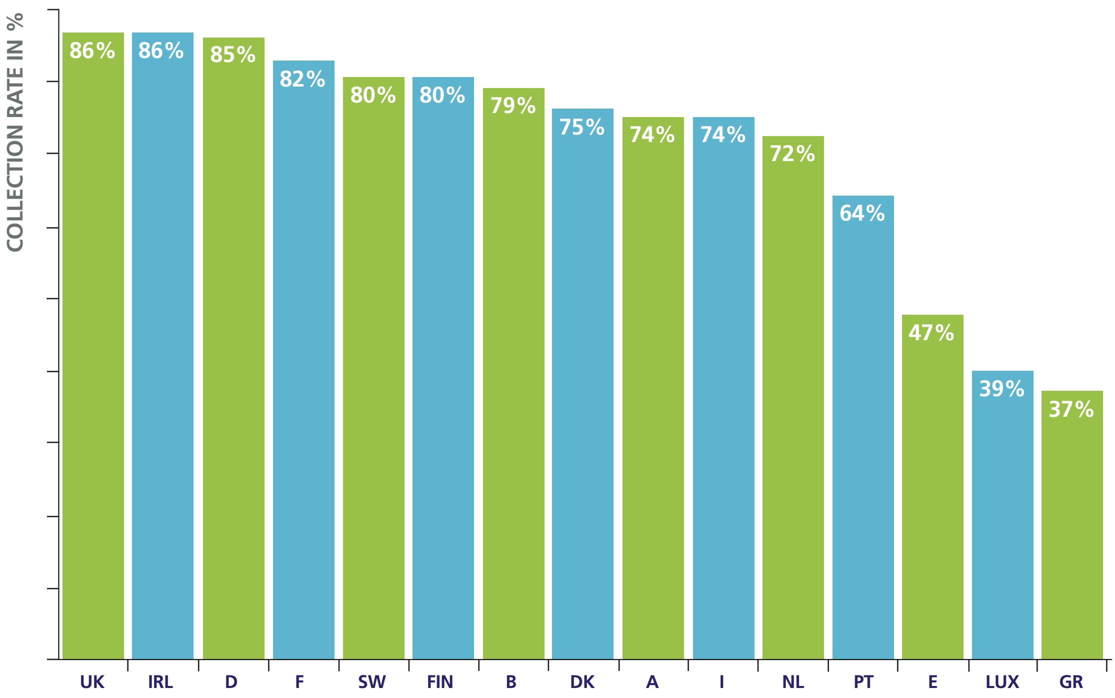


Figure 30 – Collection Rate by Country Across the EU

The main risk from improper disposal comes from 'Do-It-Yourself' oil changes, it is thought most of the uncollected 25 – 30% of used oil (or 675 kT) is from this route. However, the ability of the modern motorist to carry out this task is likely to reduce over time as engine technology advances.

As illustrated by the market data described in the introduction, lubricant volume in Europe is reducing due to smaller sump sizes and increasing drain intervals. This has the added benefit of reducing the volume of waste oil that needs to be dealt with. In future, technology improvements by both OEMs, oil marketers and additive suppliers will aid the reduction of the overall volume of waste oil in future.

Re-Refining and Re-use of Engine Oils

The overall discussions around economic and environmental benefits of reusing recycled motor oil are controversial and neither simple or straight forward. Hence the following overview focuses only on the technical realization.

The technical realization starts with a distillation process to remove fuel or other lighter components from the used oil. The next step is hydro treating, or catalytic hydrogenation to eliminate residual polymers and other chemical compounds, and finally a fractionating process which separates the oil into different grades: The lightest grades are suitable for fuel or blending into gas oil to produce heating oil, low to medium viscosity grades can be used as base oil for automotive lubricants or industrial applications, heavier materials and residues are suitable for use in heavy industry applications such as asphalt for paving. The base oils that are produced in this way are referred to as re-refined base lubricant (RRBL).

These re-refined base lubricants can then be classified as either Group I / II or III base oil under the API classification system and utilized in the development of automotive lubricants under the same strict guidelines that underpin the performance of API or ACEA quality lubricants. Thus engine oils developed using re-refined base lubricants are technically equivalent to those developed with virgin base oil.

Benefits of Lubricant Additives

Introduction

Lubricant additives packages are high performance products. Oils made from these packages are tailored to provide proper lubrication for any engine. Additionally, lubricants can be formulated for multiple applications, for example both passenger car gasoline and diesel engines. Formulation of multigrade lubricants containing polymeric viscosity modifier additives for operation in climate extremes has eliminated the need for seasonal oil changes. These lubricants provide the necessary performance to meet the vehicle manufacturer's warranty requirements, including protection of any emission control systems. Such lubricants provide confidence to the consumer and protect the owner's investment in the vehicle.

Lubricant additive technology delivers significant benefits to the consumer in controlling costs associated with vehicle design and operation. The cost of lubricant represents a small fraction of the total operating cost of the vehicle. Lubricant additives reduce consumer costs by reducing fuel and oil consumption, lowering maintenance requirements, extending service intervals, reducing downtime losses and enhancing vehicle reliability. Lubricant additives provide substantial benefits to the environment and to the end user.

The evolution of modern transportation technologies would be impossible without the development of advanced lubricant additives. A partnership approach between the original equipment manufacturers (OEMs), oil companies and lubricant additive manufacturers has permitted advances in vehicle energy efficiency, emissions reduction and vehicle systems durability.

Lubricant additives are essential ingredients in modern lubricants - performance products that help maintain engines, transmissions and aftertreatment equipment in design condition for as long as possible. This enhancement of system durability permits more effective use of energy resources, maintains low levels of exhaust emissions, and provides capabilities to employ alternative fuels, including those derived from renewable resources. A commitment to continuous advancement of lubricant additive technology facilitates the attainment of advanced engine designs to improve efficiency and conserve resources.

Fuel Compatibility

Fuel, which is produced from a variety of crude oils and different refinery processes, can have variable properties and performance. Lubricant additives are designed to cope with various types of gasoline and diesel, as well as alternative fuels, to provide engine system durability and cleanliness. Between 2000 and 2006, a significant shift has occurred within Europe in that there has been a dramatic increase in the use of diesel engines in passenger cars, driven by fuel economy concerns and the desire to reduce CO_2 emissions. In the last decade this remains stable, as shown in Table 9[28]. The consumption of diesel fuel in Europe now exceeds that of gasoline.

Table 9. Fuel Trends in Europe

% of new passenger cars using diesel fuel			
1991	2000	2006 (H1)	2014 (3Q)
15%	32%	50%	53%

Benefits of Lubricant Additives

As part of a world-wide trend, fuel sulfur levels in both gasoline and diesel have been dramatically reduced. This has been driven by concerns about the contribution to SOx emissions and also to enable the use of some exhaust gas aftertreatment systems. Lubricant additive technology, together with lubricant performance evaluation tests, has been modified to reflect the move toward low sulfur fuel and increased penetration of diesel. GTL products can also be blended into conventional oil based mineral fuel to extend the global supply and contribute to cleaner air for our cities and towns since it burns with lower sulfur dioxide, nitrogen oxide and particulate emissions.

An important recent trend is the increased use of renewable or alternative fuels. Ethanol produced from bio-mass, frequently 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[29].

Diesel fuels containing bio components such as FAMEs present special challenges in use. It is well known that FAMEs exhibit different properties to mineral diesel, including lower volatility and lower oxidative stability. It is these properties that can impact the performance required from the engine oil. Only small amounts of biodiesel mixed with mineral diesel are currently used in diesel fuel in Europe. However, fuel can pass from the cylinder to the sump via the piston rings (especially in vehicles with in-cylinder post injection). The less volatile FAME components concentrate in sump to much higher levels than found in the original fuel. This can lead to significantly increased levels of fuel dilution in the sump. Field trial data has shown that fuel containing 5% FAME (B5) can concentrate so that 50% of the fuel present is BioDiesel in the sump[30].

Whereas the addition of non-biodiesel containing Ultra Low Sulfur Diesel (ULSD) has no impact on the oxidative stability of the engine oil. The addition of different FAMEs has had a negative impact on oxidative stability and lead to viscosity increase in oxidation bench testing. However it has also been shown in oxidation testing that improved engine oil additive formulations offer increased durability in the presence of biodiesel.

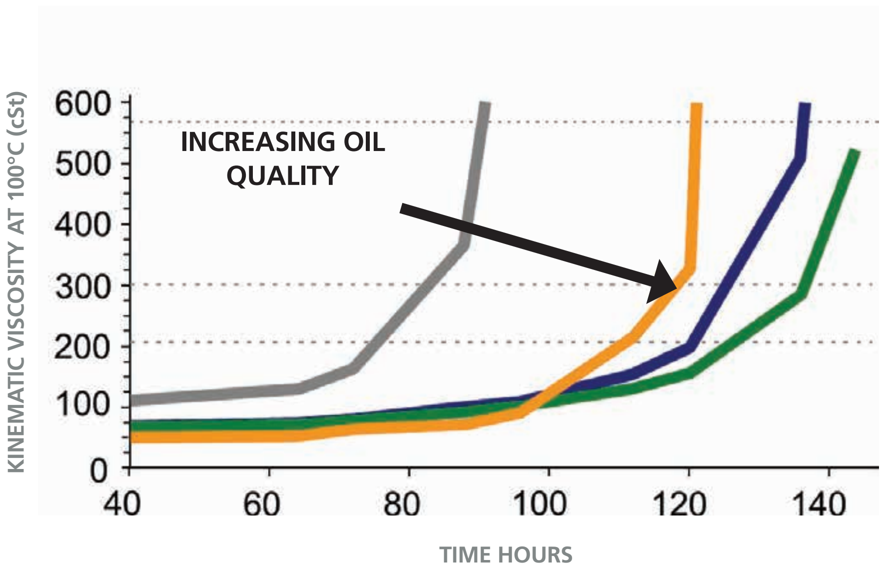


Figure 31 – Impact of Different Oil Formulations on Oxidation Performance in the Presence of Biodiesel

Corrosion is another area where the addition of bio components have been shown to have a negative impact[31]. Industry standard HTCBT (D6594) copper and lead corrosion lab testing in the presence of biodiesel has shown that increasing the percentage of biodiesel has a negative impact on copper and lead corrosion. However, additive formulations can be optimised to reduce this effect in both bench and engine testing. The use of bioethanol has been shown to have a similar negative impact on corrosion[32]. However, this is an issue that is of more concern in markets outside Europe where bioethanol use is higher.

In response to the increased use of biodiesel in the European market, ACEA specifications have been updated to include tests to ensure modern engine oils have adequate biodiesel durability. This includes the CEC-L-105[33] low temperature pumpability lab test which was added to ACEA sequences. Engine oil formulations meeting current specifications provide the required pumpability characteristics at low temperatures in the presence of biodiesel. This is in addition to various OEM lab tests which examine corrosion and cleanliness. As the ACEA sequences have evolved, many of the durability tests now use fuel containing bio components. There are also tests in development (CEC-L-104) that will specifically evaluate piston cleanliness in the presence of biodiesel. Alongside OEM oxidation bench tests, the CEC L-109[34] biodiesel oxidation bench test will also be introduced to give a baseline protection for ACEA oils.

Lubricant additive technologies have been developed to permit use of these alternative fuels[35]. Oils carrying the most up to date ACEA and OEM specifications provide protection in the market place where bio containing fuels are present. The changing landscape of alternative fuel use continues to place demands for further advances in lubricant additive design to maintain effective vehicle performance. Increasing concern over the land used for biofuel production rather than food may mean that further legislative changes are likely in future[36].

Carbon Dioxide (CO_2) Reduction and Fuel economy

A significant focus for vehicle systems design and lubrication is to enhance fuel economy, the objective being to conserve resources and reduce vehicle contributions to emissions. Road transport contributes 25% of CO_2 and other greenhouse gas emissions. The initial approach in the USA has been on Corporate Average Fuel Economy (CAFE) requirements for passenger car vehicle production. In Europe, exhaust emission legislation has been introduced including penalties for non-compliance, this was after targets were not met by the prior voluntary agreement between ACEA and the European Commission.

Table 10. CO_2 Regulations: Penalty Scheme

2007	**140 g/km** voluntary target (not met - avg. 160g/km)
2012	130 g/km (65% of new manufactured cars to meet)
2013	130 g/km (75% of new manufactured cars to meet)
2014	130 g/km (80% of new manufactured cars to meet)
2015	**130 g/km** (100% of new manufactured cars to meet)
2020	95 g/km (95% of new manufactured cars)
2021	95 g/km (100% of new manufactured cars)
	Penalties for Non compliance from 2012 onwards
	>3 g/km → 95 € / excess grams
	<3 g/km → 5 - 25 € / excess grams
	from 2019 first grammes of excess will cost 95€ each

The USA will maintain a CAFE scheme with proposed limits of 54.5 mpg for cars and light trucks by 2025; while in Japan a CAFE style scheme is proposed which would raise automotive FE standards 24% by 2020 vs. 2009.

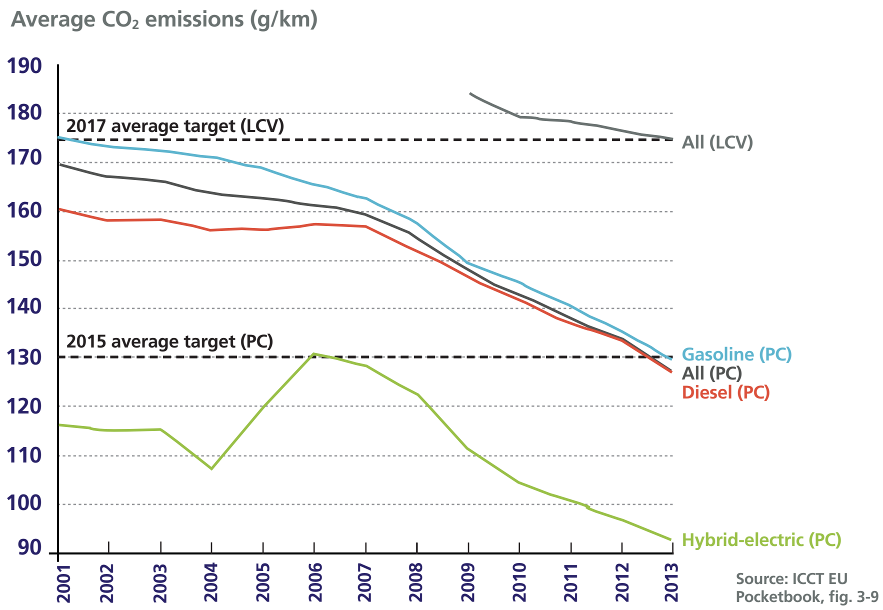


Figure 32 - Average CO_2 Emissions of Vehicles Over Time Compared to EU Targets

In addition to demands from the consumer to control fuel consumption, reduce operating costs and increase vehicle performance, European and US lubricant testing puts significant emphasis on fuel economy performance. This has resulted in fuel economy enhancements from the lubricant. Many OEMs have introduced fuel economy requirements in their in-house specifications based on the CEC M111[37] fuel economy test and other tests. Examples of these requirements are given in Table 11.

Table 11. FE Requirements, Industry and OEM

FE requirement in industry and OEM tests	
Specification	FE requirement
ACEA A1/B1, A5/B5, C2	2.5%
ACEA C3	1.0%
BMW	1.0%
Daimler	1.0 or 1.7%
Ford	2.5, 3.0 or 3.3%
JLR	3.0, 3.3 or 3.8%
GM Opel	1.5%
Renault	1.0% or 2.5%
PSA	1.0, 2.5, 3.0 %
VW	2.0%

Fuel economy improvement has become one of the key drivers for change in lubricant technology. Lubricant additives are a key enabler for the engine manufacturers to meet the demands of both legislators and consumers for passenger and light duty vehicles whilst in the heavy duty diesel market the need to cut the cost of vehicle ownership is also driving the development of new lubricant additive technologies to deliver fuel efficiencies.

In North America, the new PC-11 heavy duty diesel category introduces a new low viscosity sub category to deliver fuel economy benefits whilst not compromising on engine durability. In Europe commercial vehicle manufacturers use in house fuel economy tests and on road field trials to ensure adequate fuel economy of their oils.

Reducing energy loss due to friction in the engine is key to improving the fuel economy performance of vehicles; this has driven the trend towards lower viscosity oils, which reduce engine friction, and for formulations which use innovative new additive technology to lower power loss due to friction and deliver increased fuel economy.

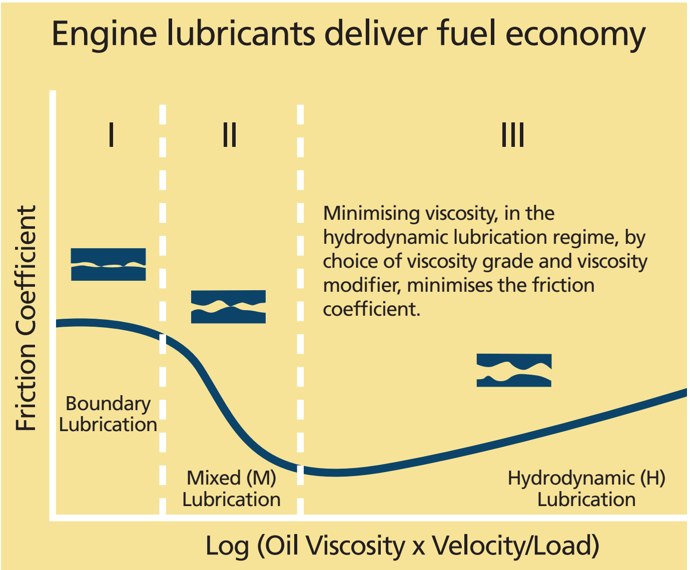


Figure 33 - Stribeck Curve Showing Different Lubrication Regimes

New viscosity modifier technologies are being deployed in these low viscosity lubricants which are designed to contract at lower engine operating temperatures such that the oil has a lower viscosity during the warm up phase of engine operation. Additionally friction modifying and surface active technologies like molybdenum dithiocarbamate and glycerol mono oleate are being increasingly deployed to deliver the required efficiencies. The chemistries and mode of action of these fuel economy technologies is discussed in detail in the Chemistry of Lubricant Additive section of this document.

SAE J300[38], the standard which defines the limits for classification of engine oil in rheological terms has recently been updated to include viscosity grades which cover SAE 16, SAE 12 and SAE 8 with minimum HTHS viscosities of 2.3, 2.0 and 1.7 mPa-s respectively. The benefit of establishing these new viscosity grades is to provide a framework for formulating lower HTHS engine oils in support of improved fuel economy.

SAE Viscosity Grade	Low-Temperature (°C) Cranking Viscosity(3), mPa·s Max	Low-Temperature (°C) Pumping Viscosity(4) mPa·s Max with No Yield Stress(4)	Low-Shear-Rate Kinematic Viscosity(5) (mm^2/s) at 100°C Min	Low-Shear-Rate Kinematic Viscosity(5) (mm^2/s) at 100°C Max	High-Shear-Rate Viscosity(6) (mPa·s) at 150°C Min
OW	6200 at -35	60 000 at -40	3.8	-	-
5W	6600 at -30	60 000 at -35	3.8	-	-
10W	7000 at -25	60 000 at -30	4.1	-	-
15W	7000 at -20	60 000 at -25	5.6	-	-
20W	9500 at -15	60 000 at -20	5.6	-	-
25W	13 00 at -10	60 000 at -15	9.3	-	
8	-	-	4.0	<6.1	1.7
12	-	-	5.0	<7.1	2.0
16	-	-	6.1	<8.2	2.3
20	-	-	6.9	<9.3	2.6
30	-	-	9.3	<12.5	2.9
40	-	-	12.5	<16.3	3.5 (OW-40, 5W-40, and 10W-40 grades)
40	-	-	12.5	<16.3	3.7 (15W-40, 20W-40, 25W-40 grades)
50	-	-	16.3	<21.9	3.7
60	-	-	21.9	<26.1	3.7

1. Notes - 1mPa·s = 1 cP; 1 mm^2/s = 1cSt
2. All values, with the exception of the low-temperature cranking viscosity, are critical specifications as defined by ASTM D3244 (see text, Section 7.)
3. ASTM D5293: Cranking viscosity - The non-critical specification protocol in ASTM D3244 shall be applied with a P value of 0.95.
4. ASTM D4684: Note that the presence of any yield stress detectable by this method constitutes a failure regardless of viscosity.
5. ASTM D445.
6. ASTM D4683, ASTM D4741, ASTM D5481, or CEC L-36-90.

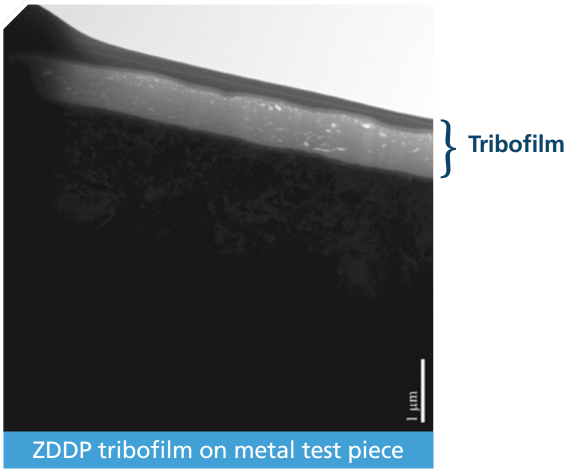
Figure 34. SAE J300 Oil Classification

Whilst these new lower viscosity lubricants have been able to deliver fuel economy benefits, the viscosity must be high enough so that the oil can form a continuous film at high temperatures in order to protect the engine from wear and deliver the engine durability requirements of the manufacturers[39].

Durability and Protection

Lubricant additives have a direct role in protecting engine parts and maintaining engine performance throughout the drain interval. As described in the Chemistry of Lubricants Section, many of the components are surface active and are designed to interact directly with engine parts or contaminants created as by-products of combustion. Via this direct action on the different surfaces in the engine, additive components prolong the life of components and therefore the overall engine lifetime and reliability. The additive types are designed to interact with specific surfaces. By careful formulation and balancing of different additive types, the overall required durability performance is achieved.

Many of the components within an engine oil additive act directly upon engine parts and form protective layers. The most historically important and well studied is ZDDP (zincdialkyldithiophosphate)[40], the chemical structure of which is discussed in detail in the Chemistry section. ZDDP was originally used as an antioxidant but its antiwear properties were also quickly noted and it has become ubiquitous in engine oil formulations. As analytical techniques have advanced, the mechanism of ZDDP action has been studied in detail. It is known to form a mechanically strong, relatively thick protective layer of polyphosphate glass on ferrous surfaces within the engine. This is thought to act as a protective barrier that prevents adhesion between metal surfaces. This film is long lived and most of the wear is likely to be taking place within the tribofilm rather than on the engine parts themselves. This is illustrated in the image below which shows the protective layer formed on a metal test piece. As surfaces within the engine change and advance, formulations will have to adapt to provide the same protection in modern engines.



The engine oil is exposed to very high temperatures during operation, this is especially true of modern engines that are smaller with a higher power density and also often turbocharged. The turbocharger can reach temperatures in excess of 350°C and is often the hottest area of the engine that the oil is exposed too (even though it may only be for short periods of time). To provide adequate durability in this environment additives are formulated with the correct level of antioxidants, detergents and dispersants to prevent deposits forming around the turbocharger bearing. This is illustrated in the images below. Additive formulation can have a key role in providing durability required in these very high temperature engine components.

Figure 35. ZDDP Tribofilm on Metal Test Piece

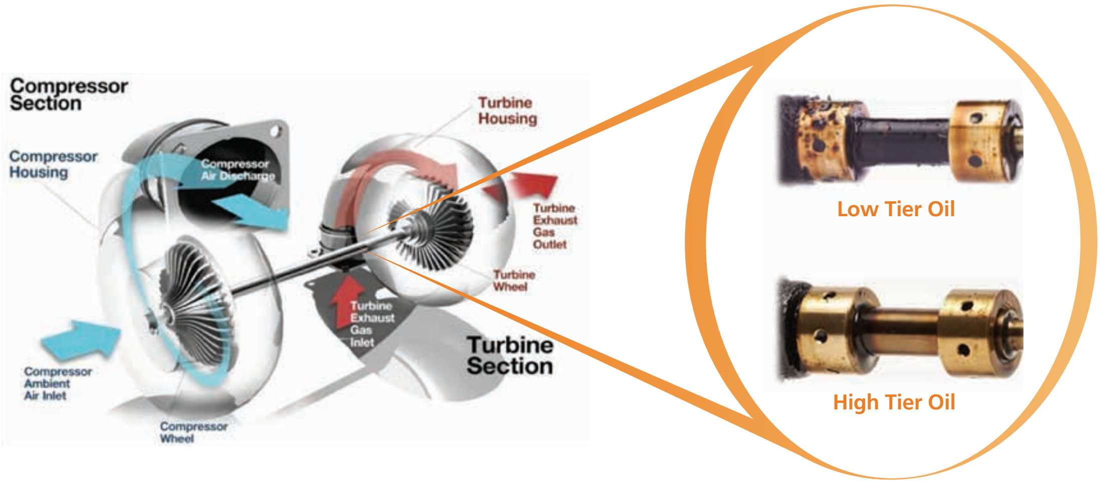


Figure 36. Example of Turbocharger Deposits with Different Oil Qualities

The durability of the additive package also has an impact on long term vehicle durability. Recent studies have shown that using an oil with less than adequate sludge protection in a poor fuel environment can have serious implications for the vehicle[41]. Field trial data indicated that repeated use of a low durability oil can shorten drain interval and have a cumulative impact on engine reliability and performance (illustrated in Fig 37).

Benefits of Lubricant Additives

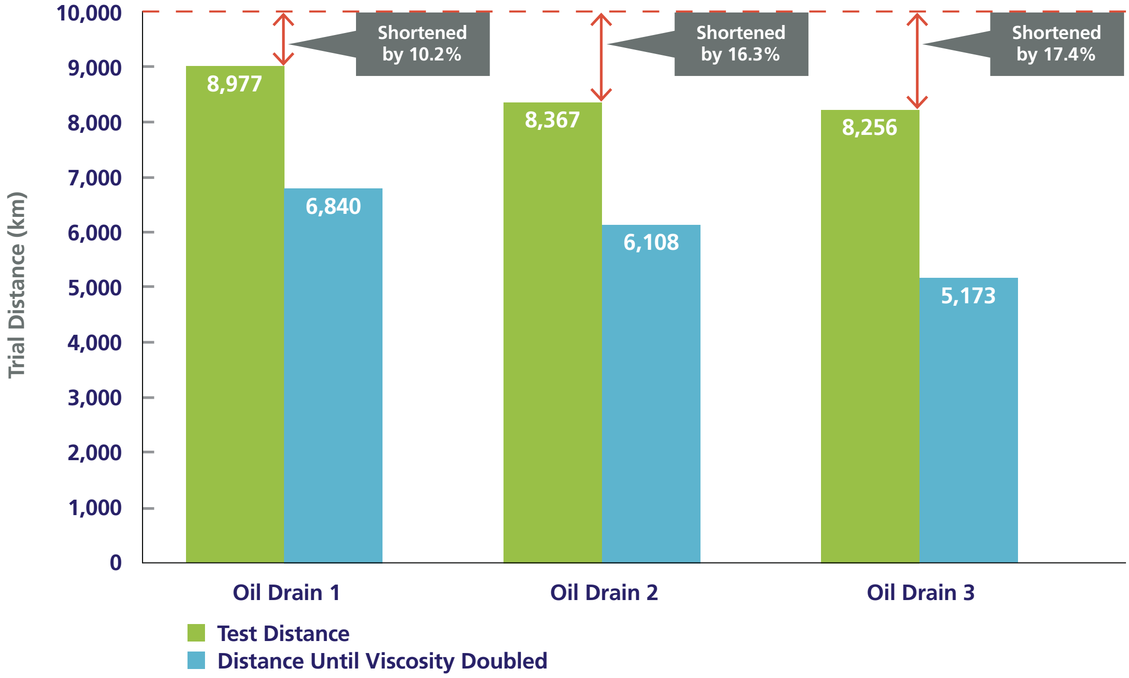


Figure 37. Long term Effects of Using an Oil with Low Durability

This study also showed that the lack of oil durability over several drain intervals lead to many serious failure modes (oil filter blocking, sensor faults and bearing failures).

The additive formulations play a large role in the protection of the engine. Without adequately formulated additives there can be very serious consequences for the overall engine reliability. This is a key benefit of the use of lubricant additives is their protective capabilities. The improving durability performance of modern additive formulations enables OEMs to enhance the efficiency of modern engines while ensuring durability is not sacrificed.

Lubrication Engineering

Lubricant additives are now considered as lubrication engineering design components. Lubricant additives are designed and optimised in the development process to meet the performance requirements of the engine. Additives are designed to control:

- Chemical oil parameters: oxidation resistance, high temperature resistance, oil thickening by viscosity increase, low temperature flow viscosity, shear stability, seal compatibility, low volatility, foam inhibition, soot dispersion, and corrosion control
- Physical oil parameters: wear resistance, maintain oil film thickness, friction reduction, compatibility with after treatment devices, heat transfer, sludge and deposits handling.

Lubricant additive development has permitted extended oil drain service intervals, enhanced fuel efficiency and improved engine durability.

In conclusion, the contribution that lubricant additive have made in the above areas may most effectively be illustrated by considering the advances in engine design that have been achieved over the last few decades. In order to meet the latest emission regulations and the demands of the consumer for lower cost of ownership, OEMs have designed more fuel efficient engines which deliver higher power output and at the same time have extended oil drain intervals. These elements have all lead to a significant increase in the stress on the lubricant.

Table 12. Example of Changes in Passenger Car OEM Hardware

Factors	1996	2014	Change and Impact
Engine	2.3L Gasoline	2.0L Gasoline	-15% smaller
Power	148 HP	220 HP	+48% more power
Power Density	64 HP/litre	110 HP/litre	+72% power density
Emissions	Euro II	Euro VI	Reduced Emissions
Weight	1147 kg	1407 kg	+23% heavier
0 – 100 km/hr	8.2 s	6.5 s	More performance

Table 13. Example of Changes in Heavy Duty OEM Hardware

Factors	2004	2014	Change and Impact
Engine	15.9L V8	12.8L Inline 6	-20% lighter
Power	510 HP	510 HP	Maintained power
Power Density	32 HP/litre	40 HP/litre	+25% power density
Emissions	Euro IV	Euro VI	Reduced Emissions
EGR Rate	High	Low	Soot changes
Oil Drain	100,000 km	150,000 km	Increased need for durability

Tables 12 and 13 show generational advances of typical gasoline passenger car and commercial vehicle. This documents the specific power output increases over time and illustrates the advances that have been achieved by the OEMs and highlights the increase in stress on the lubricant. The capability to absorb this increased stress on the lubricant over the period is largely attributable to advanced additive technology.

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