A SECTOR GROUP OF cefic

LUBRICANT ADDITIVES

and

THE ENVIRONMENT

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Lubricant Additives and the Environment

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 15 countries of the European Community (EU-15).

The first edition of this study was prepared in 1993 and was conducted to develop information which was not previously available, with the purpose of putting in perspective the benefits to the environment and the end-user provided by lubricant additive technology. This edition (2007) updates the information and reanalyses the data.

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 environmental fate of crankcase lubricant additives is explored, and a mass balance from cradle to grave is presented.

INTRODUCTION

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

The petroleum additive industry is developing technologies and materials for the supply of service products for engines and motor vehicles, in co-operation with the petroleum and automotive industries, amongst others.

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 impact on the environment.

Aim

The aim of this paper is to introduce ATC, to explain how the association operates, and to demonstrate the contribution lubricant additives make towards industry, the consumer and ultimately the environment.

By answering questions, the paper hopes to allow industry and regulators to focus on the priorities for future attention rather than things which are trivial or already well known.

Scope

The document confines itself to a study of automotive crankcase oil additives, their chemistry, the benefits they provide and their fate in the environment. Automotive crankcase oil additives comprise those used in passenger car diesel and gasoline engine lubricants (PCMO - passenger car motor oil) and in bus and truck diesel engine lubricants (HDDO - heavy duty diesel oil).

The study is based mainly on the 15 European Community members (as of April 2004) comprising Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxemburg, Netherlands, Portugal, Spain, Sweden and the UK. This choice was based on the availability of the widest range of data to allow cross checking for consistency.

ATC

The Technical Committee of Petroleum Additive Manufacturers in Europe (ATC) was established in 1974 for member companies to discuss topics of a technical and statutory nature which were a concern to their industry. The current members are shown in Table 1. Further information about ATC can be found on the website www.atc-europe.org.

Afton Chemical
Baker Petrolite
BASF
Chemtura Corporation
Chevron Oronite
CIBA Specialty Chemicals
Croda
Evonik RohMax Additives GmbH
Infineum
Innospec Fuel Specialties
Lubrizol
Rhodia

Table 1. Members of ATC

Membership is open to all additive companies which operate chemical processes for the manufacture of petroleum additives, or have comprehensive test facilities in Europe.

In 1979, ATC became affiliated as an industry sector group of Cefic, a federation of associations representing European chemical manufacturers.

ATC organisation and objectives

The ATC organisation comprises a main committee and sub-committees responsible for

- Health, Safety and Legislation
- Lubricant Performance Testing
- Fuels
- Quality Monitoring
- External representation and strategy

In addition, the Technische Vereinigung für Mineralöl-Additive in Deutschland e.V. (TAD) co-ordinates activities for ATC in Germany.

The objectives of ATC are:

- To provide a forum for additive companies to meet and discuss developments of a technical and/or statutory nature concerning the manufacture or application of additives in fuels, lubricants and other petroleum products.
- To ensure dissemination of ATC views to related international and national technical groups and organisations.
- To participate in work of a technical nature in conjunction with associated industry or statutory organisations or groups.

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. More recently ATC has actively participated in discussions on aspects of environmental legislation including REACH (Registration Evaluation and Authorisation of Chemicals).

By communicating with associated industries and 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 about the petroleum additive industry are:

- World-wide the industry spends about €400 million/annum (2005) on research and development, of which €115 million is spent in Europe (EU-23).
- World-wide the industry has a turnover of about €7,000 million of which the European market is about €1,900 million.

- The industry employs directly about 2,800 people in Europe and about 8,400 globally.
- The industry operates more than 25 research and development establishments and manufacturing sites in Europe, and more than 75 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.

The automotive crankcase lubricant additive business

All automotive crankcase lubricants need additives, at total concentrations (as sold) of typically 10 - 30%. Lubricant additives help provide the performance necessary for efficient operation and prolonged engine life.

No single additive component can do everything. Several additive components are needed to deliver the performance required. Performance requirements change as engine design, operating conditions, legislation, and source of supply and processing methods of the base oil change. Several additive components of different chemistry 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. The customer (an oil company) specifies the performance requirements of the finished lubricant. The petroleum additive supplier evaluates combinations of additive components until the required performance is achieved. The additive package is then offered for sale without disclosing proprietary details of its composition.

Development of a new lubricant

New lubricants are developed to meet both changes in, and new, Original Equipment Manufacturer (OEM) needs, or consumer requirements. For example, a new engine design configuration may require improved lubricant performance. Equally, a different service application or lubricant drain interval may require changes in lubricant performance. These requirements are identified and new or existing engine tests and other evaluations of physical characteristics or performance properties may be prescribed to ensure these requirements are met.

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 then carry out the engine tests necessary to develop the lubricant. 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 additive package) will be offered for sale thereby satisfying the OEM and market-place need.

Cost, complexity and confidentiality

The costs of engine testing are high because comprehensive documentation and statistically valid data are required. For example, the engine test development costs for a crankcase lubricant suitable for use in today's European and US diesel and gasoline engines are at least €1 million. This presumes the existence of a considerable background 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). Apart from running engine tests, extensive field tests in vehicles, often extending to millions of kilometres, are needed to guarantee performance.

To meet the ever-changing needs of the engine designer and of the consumer, always with respect to environmental concerns, the additive industry puts a major effort into developing the products it sells. 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 €115 million/year in EU-23 on new developments. A single component can cost between one and ten million Euros to develop and the cost of development plus that of the manufacturing plant can take ten to fifteen years to recover. The cost of compliance with health and safety legislation has risen over the years, and will increase still further when REACH is 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 developments. Improvements in fuel economy alone will require additive developments to meet 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 be readily patentable. Therefore, many such inventions are treated as proprietary compositions without additional patent protection.

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 satisfy both this requirement and the current legislative requirement for disclosure of hazardous ingredients on the Safety Data Sheet (SDS), the ATC has established an international nomenclature system describing chemical ingredients in terms of their key functional groups[1]. This nomenclature ensures that accurate and unambiguous health and safety information on all products can be provided which is recognised by industry downstream users and emergency personnel worldwide[2]. This nomenclature system is also used by international regulatory bodies.

HISTORY OF ADDITIVES DEVELOPMENT

The pre-additive period – until 1932

Until the 1930s crankcase 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 were becoming more sophisticated. Engine oils were becoming more stressed, giving rise to a need for additives.

The main steps of lubricant additive development - 1930s to the present

Figure 1 gives a chronological view of the development of the main additive families[3,4,5,6,7,8,9,10,11,12,13]. 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.

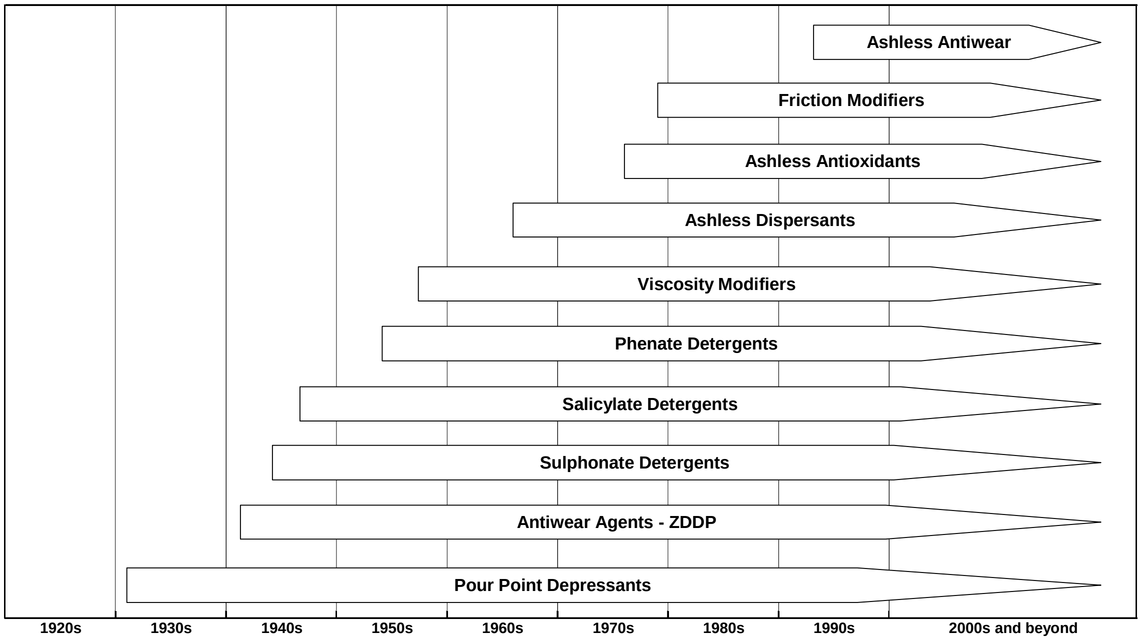


Figure 1. Development of lubricant additives

Main additive component families

- Pour point depressants (1932)
- Zinc dialkyldithiophosphates (ZDDP) antioxidant /antiwear agents (1940)
- Detergent sulphonates and salicylates (1940s)
- Detergent phenates (1950s)
- Polymeric viscosity modifiers (1950s)
- Ashless dispersants (1960s)
- Inhibitors (1970s)
- Friction modifiers (1970s)
- Ashless antiwear (1990s)

Further diversification within each additive family continues. This development is driven by new lubricant specifications, which in turn are driven by evolution in engine design to meet more stringent emissions legislation and increasing consumer demands.

Main crankcase oil classification currently used in Europe

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

Functions of engine oils and additives

- **Friction reduction** between moving surfaces - preventing metal to metal contact which leads to rapid wear, and at the same time preventing loss of useful energy through heat due to excessive friction.
- **Corrosion protection** of the engine parts - by inhibiting chemical attack from a wide variety of contaminants (water, acidic combustion products, particulate matter, etc.)
- **Heat transfer** by acting as a coolant. Lubricants remove heat generated by friction, the combustion process and other sources, by transfer from contact with substances at higher temperatures.

- **Operating at extremes of temperature -** the highest occur under high engine loads and high outside temperatures; the lowest at cold engine start at low outside temperatures.

- **Engine seals protection** to avoid oil leakage and ground contamination.

- **Suspension of crankcase oil contaminants** such as combustion by-products and wear debris until removed by the oil filter. Small particles are dispersed in the lubricant, and engine parts are kept clean.

- **Ensure continued efficient performance** of exhaust gas after treatment systems.

Base oils or synthetic base stocks alone cannot provide all the engine lubricant functions required by a modem gasoline or diesel engine. Over the last eighty years a number of chemical additives have been developed (Figure 1) to enhance base stock properties, overcome their deficiencies and provide the new performance levels required by the technological evolution of engines or by new regulations. As base oils continue to evolve with increased use of hydrofinishing and hydrocracking at the refining stage, along with new production methods such as Gas to Liquid (GTL), the additives required will continue to evolve in parallel.

These developments have led to a wide range of base stock classifications, Groups I to VI, based on the saturates level, sulphur content and viscosity index (VI) properties of the oil (Figure 2).

CHEMISTRY OF LUBRICANT ADDITIVES

Lubricant additives fall into two categories:

- those protecting metal surfaces in the engine, such as antiwear, anti-rust, anticorrosion and friction modifier additives; and,

- those reinforcing base stock performance, such as antioxidants, dispersants, viscosity modifiers and pour point depressants.

Detergent additives play a part in both areas.

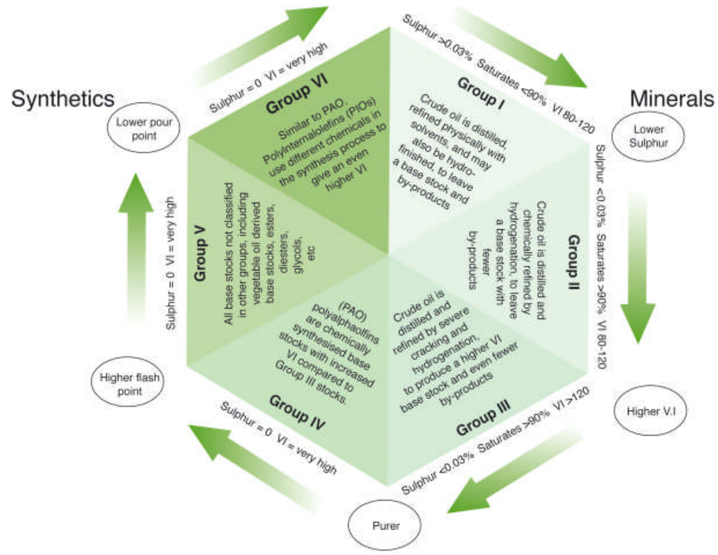


Figure 2. Base stock classification

Oil soluble materials

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 3). Since the two parts of the molecule have different solubilities in oil, additives therefore tend to exist colloidally as inverse micelles.

Figure 3. 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.

- Sulphonates (Figure 4)

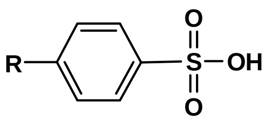


Figure 4. General structure of a sulphonate based detergent

- Phenates (Figure 5)

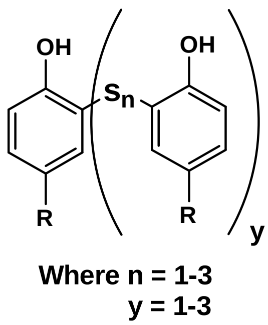


Figure 5. General structure of a phenate based detergent

- Salicylates (Figure 6)

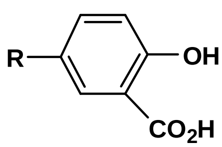


Figure 6. Typical structure of a salicylate based detergent

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 (Figure 7). 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 (Figure 8).

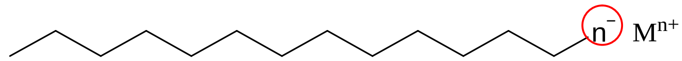


Figure 7. Neutral detergent

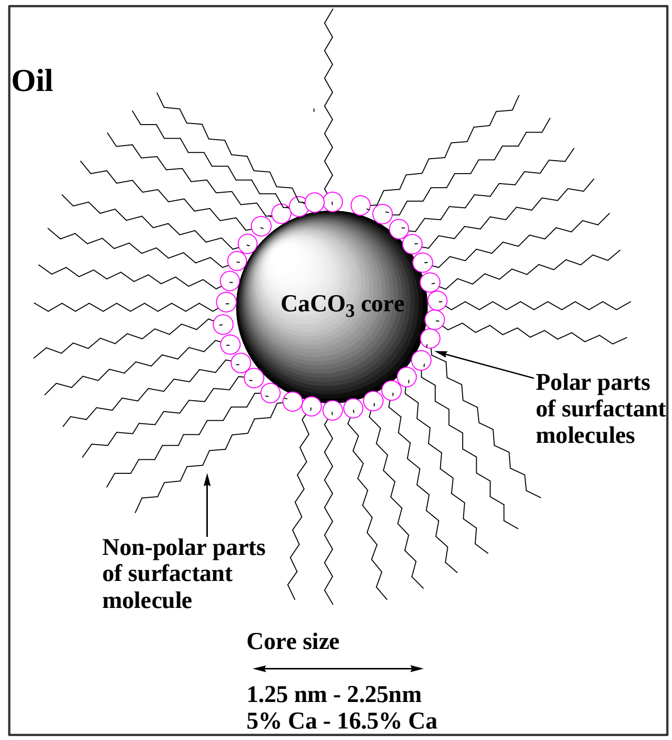


Figure 8. Overbased detergent

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.

Mode of action

Detergents reduce or remove 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)

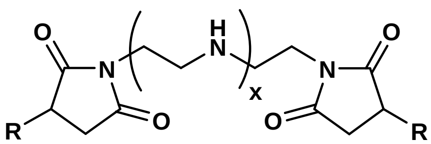


Figure 9. General structure of a succinimide based dispersant

- Succinic esters of polyols (Figure 10)

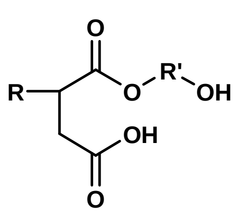


Figure 10. General structure of a succinic ester of polyols

- Mannich bases (Figure 11)

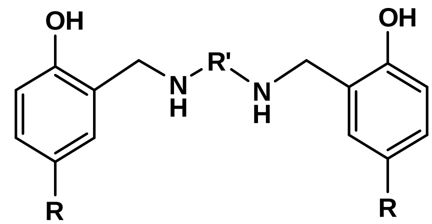
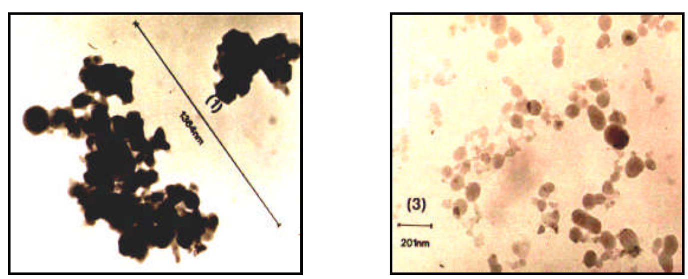


Figure 11. General structure of a Mannich base

Mode of action

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 sulphurised 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 2). 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.

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

Table 2. Performance parameters of different ZDDP types

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

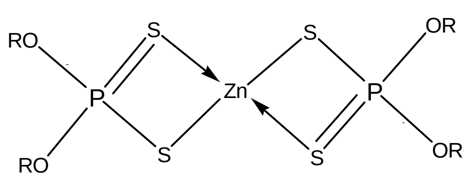


Figure 13. Zinc dialkyl dithiophosphates

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.

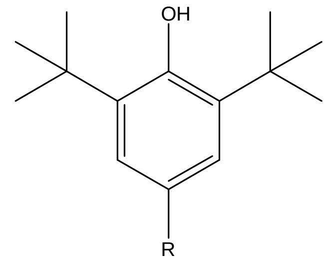


Figure 14. Hindered phenol

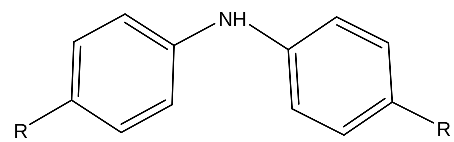


Figure 15. Diphenylamine

Figure 16 shows representative phosphorus compounds used as inhibitors.

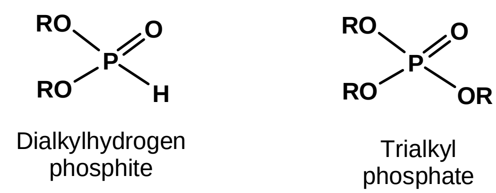


Figure 16. Phosphorus based inhibitors

Modes of action

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.

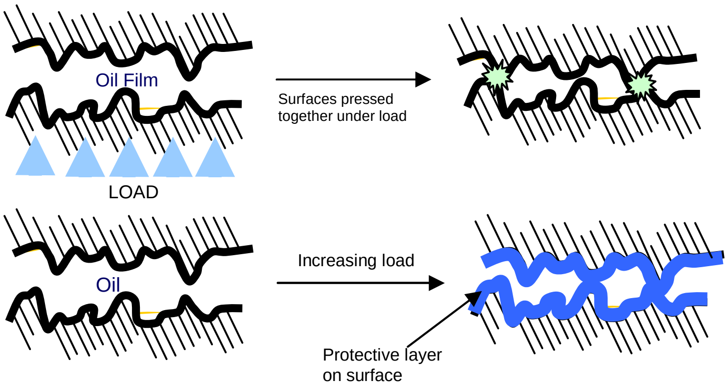


Figure 17. Illustration of boundary lubrication

Initiation:
$$RH \longrightarrow R^{\bullet}$$

Propagation:
$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$
$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$
$$ROOH \longrightarrow RO^{\bullet} + HO^{\bullet}$$
$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}$$
$$HO^{\bullet} + RH \longrightarrow R^{\bullet} + H_2O$$

Termination:
$$R^{\bullet} + ROO^{\bullet} \longrightarrow ROOR$$
$$R^{\bullet} + R^{\bullet} \longrightarrow R\text{-}R$$

Figure 18. Oxidation chain reaction

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 and left unchecked increases 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.

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.

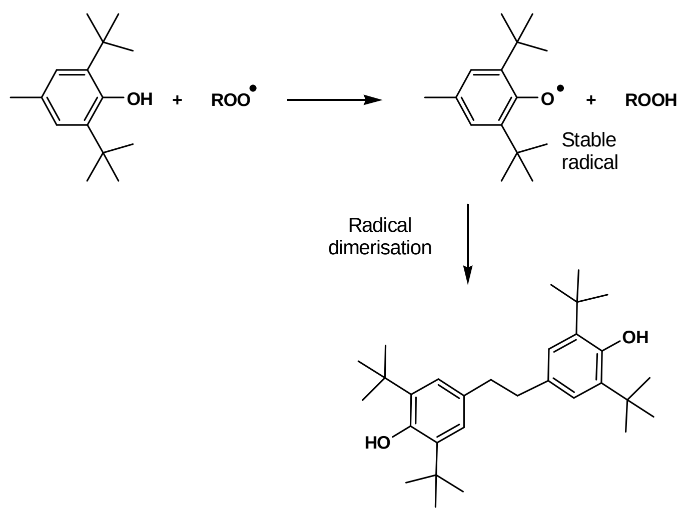


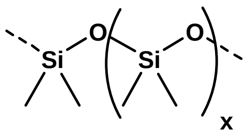
Figure 19. Radical Trapping by Hindered Phenols

Aromatic amines have a complementary mode of action to that of the phenolic family[14].

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 (Figure 20) are very commonly used as antifoam agents.



Polymethyl siloxane antifoam

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 etc. 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:

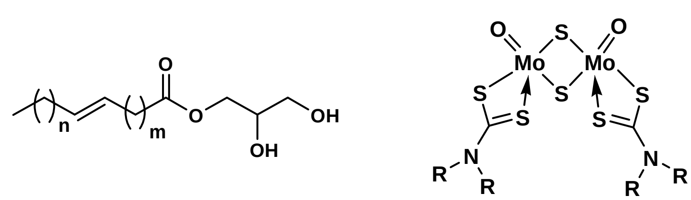
- Amines, amides and their derivatives
- Carboxylic acids or derivatives
- Phosphoric or phosphonic acids and their derivatives.

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 disulphide 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:-

- Sulphurised 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)



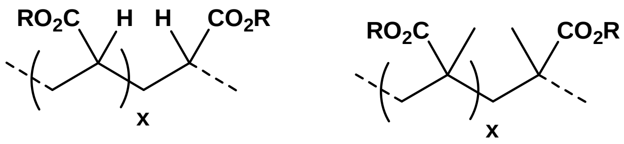
GMO MoDTC

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 the polyacrylates and the polymethacrylates (Figure *22*).



Polyacrylate   Polymethacrylate

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. This entails meeting, simultaneously, the limits for low-temperature W-grades (determined with a Cold Cranking Simulator (CCS) and Mini Rotary Viscometer (MRV)) and high-temperature grades (kinematic viscosity at 100°C). 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 l0W40). 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. Multigrade oils have a lower viscosity at low temperatures allowing easier cranking and starting than the corresponding monograde oil and as a result improved fuel consumption. These effects are shown schematically in Figure 23.

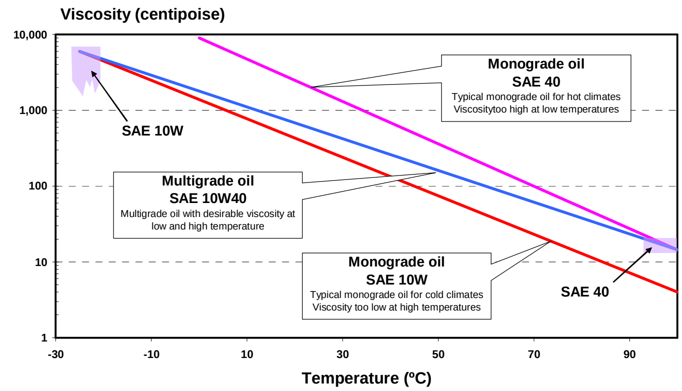
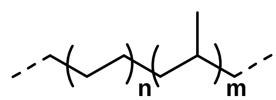
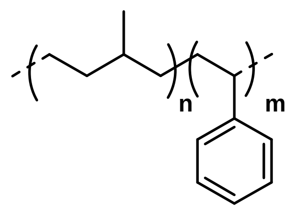


Figure 23. Effects of temperature on viscosity

Higher molecular weight polymers (from 50,000 to 500,000) 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.



Ethylene-propylene copolymer (OCP)



Hydrogenated styrene isoprene copolymer

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 50 % 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 23). In addition to their ability to modify oil viscosity, viscosity modifiers can provide other functions such as 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. In recent years heavy duty diesel soot handling has become one of the key issues for lubricant and engine performance as the drive to increase oil drain intervals has grown. Some dispersant viscosity modifiers exhibit excellent soot handling and improved wear control, the latter being due to a reduction in abrasive wear.

Components and performance packages

Finished crankcase 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 crankcase lubricants, is usually purchased and blended separately by the lubricant marketer. Figure 25 illustrates this schematically.

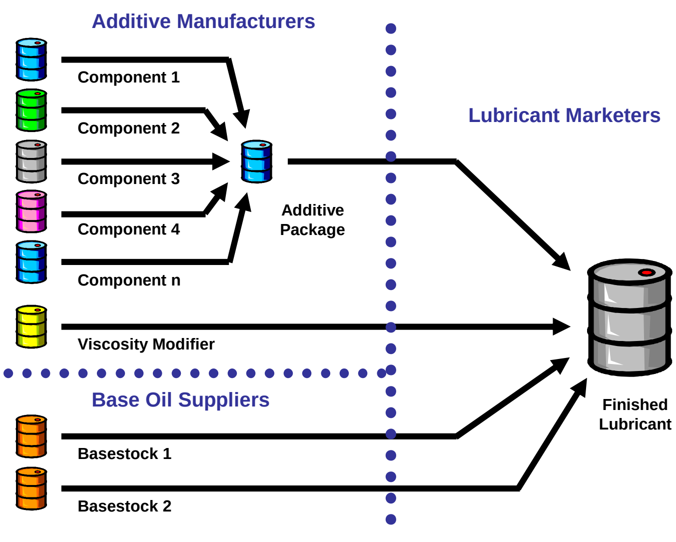


Figure 25. Component and package formulation

A performance package is therefore a concentrate of several components (5 to 10 or even more) blended carefully together. Adjusting a performance package is not easy. 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 formulated correctly. The development of a performance package is technically challenging and expensive, requiring considerable expertise.

BENEFITS OF LUBRICANT ADDITIVES TO ENVIRONMENT AND CONSUMER

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.

Petroleum conservation

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 including cracking and hydrotreating to produce higher quality basestocks. Some high performance formulations incorporate chemically manufactured hydrocarbons such as polyalphaolefins (PAO) and esters. The basestocks are classified as shown in Figure 2.

Base stock properties can differ markedly depending on the source of crude and the refining process. Lubricant additive technology can provide 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.

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. Within the past decade 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, as shown in Table 3. The consumption of diesel fuel in Europe now exceeds that of gasoline[15].

% of new passenger cars using diesel fuel Source: AID Newsletter[16]		
1991	2000	2006 (1st half)
15%	32%	50%

Table 3. Fuel trends in Europe

Alternative Fuels

As part of a world-wide trend, fuel sulphur 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 sulphur fuel and increased penetration of diesel.

A variety of alternative fuels are being actively investigated to develop cleaner energy sources for transportation, to use renewable resources, and to reduce emissions. Significant further shifts are anticipated in the fuel market-place in Europe, with movement towards fuels containing oxygenates, bioethanol and biodiesel. Longer term the use of gas-to-liquid (GTL), biomass-to-liquid (BTL) and other alternative fuels is expected to increase. The environmental impact of these alternatives is under active investigation.

Lubricant additive technologies are being developed to permit use of these alternative fuels[17]. These shifts continue to place demands for further advances in lubricant additive design for the effective performance of vehicles operating on these fuels.

Fuel economy

A significant focus for vehicle systems design and lubrication is to enhance fuel economy, the object being to conserve resources and reduce vehicle contributions to emissions. Road transport contributes 14% of greenhouse gas emissions[18]. The initial approach in the USA has been on Corporate Average Fuel Economy (CAFE) requirements for passenger car vehicle production. In Europe, no fuel economy improvements have yet been mandated. However, ACEA has reached a voluntary agreement with the European Commission to reduce CO_2 emissions to a target of 140g CO_2/km by 2008, and a further reduction to 120g CO_2/km is envisaged for 2012 (Figure 26). In addition demands from the consumer to control fuel consumption, reduce operating costs and to increase vehicle performance have resulted in fuel economy enhancements from the lubricant. European and US lubricant testing puts significant emphasis on fuel economy performance. Some OEMs have introduced fuel economy requirements in their in-house specification, based on the CEC M111 fuel economy test[19] and other tests. These requirements are given in Table 4.

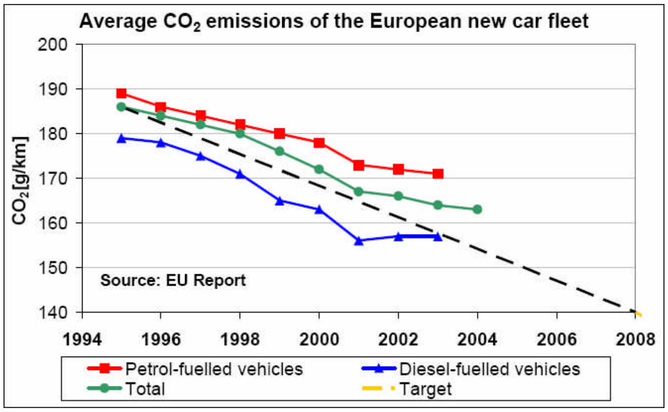


Figure 26. Fuel economy requirements (Source: Ricardo)

FE requirement in CEC L-54 (M111E) test, industry and OEM	
Specification	**FE requirement**
ACEA A1/B1, A5/B5, C1	2.5%
ACEA C3	1.0%
BMW*	1.0%
Daimler	1.0 or 1.7%
Ford	2.5 or 3.0%
Opel*	1.5%
Renault	1.0%
VAG*	2.0%
* OEM test method	

Table 4. FE requirements, industry and OEM

Lubricant additives play a role in fuel economy. Friction modifiers reduce energy loss due to engine friction. The viscosity modifier reduces viscous drag in engine operation, enhancing efficiency. Antioxidants control lubricant viscosity, and together with detergents and dispersants which maintain system cleanliness, help retain vehicle fuel economy characteristics.

Lubricant consumption control

In addition to significant contributions to fuel economy, conservation of petroleum resources, with attendant reduced contribution to emissions, is achieved by enhancing lubricant economy in service (Table 5). Modern, low emission engine designs create significant lubrication challenges for additive chemistry to control deposits and wear, and maintain long-term low emissions performance. The combination of reduced oil consumption and extended drain intervals greatly increases the load on the lubricant[20] (Figure 27).

Lubricant additives assist in reducing oil consumption by modifying the physical properties of the lubricant such as viscosity, and enable the use of less volatile base fluids. Maintaining systems integrity is a key function of the lubricant. Losses due to leakage have been almost eliminated with the help of oil-seal compatible lubricants.

Vehicle Engineering and Lubricant Additive Development Higher performance, with reduced lubricant quantity for gasoline passenger cars (data based on top specification engines)				
Model year	1949	1972	1992	2005
Power (kW)	25	74	96	120
Power density (kW/L)	21	37	45	60
Oil fill (L)	3.0	3.7	3.5	3.5
Oil consumption (L/1,000km)	0.5	0.25	0.1	0.1
Oil change interval (km)	1,500	5,000	15,000	30,000
Oil flush at oil change	Yes	No	No	No
Total oil used after 30,000km (L)	87.0	29.8	10.0	6.5
Average fuel consumption (L/100km)	12	10	7	7
Engine durability (1000km)	<100	175	250	250
Source: Ricardo				

Table 5. Engine oil use trends

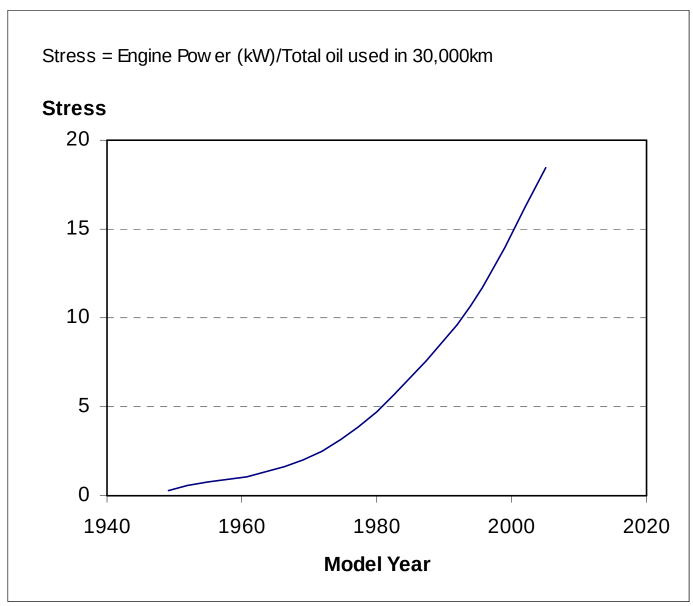


Figure 27. Stress on passenger car lubricant

Additive components also help control wear and deposits, maintaining low oil consumption throughout a vehicle's life.

Lubrication engineering

Lubricant additives are now considered as lubrication engineering design components. Appropriate lubricant development enables new engine system designs to perform successfully.

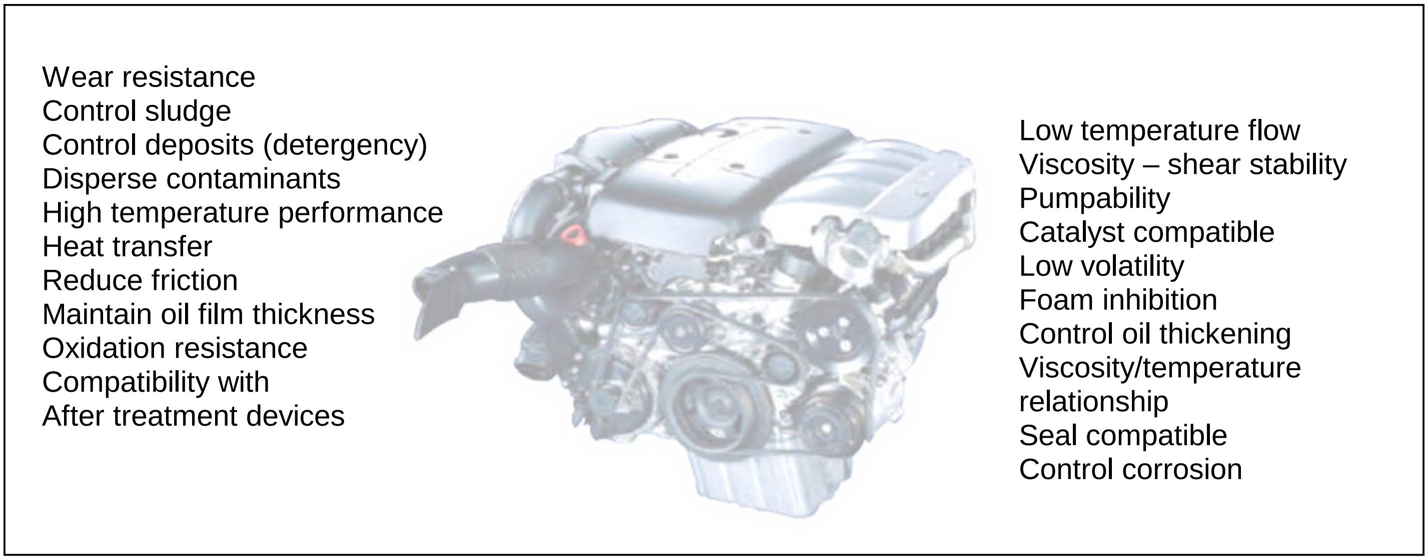


Figure 28. Lubricant additives as design components

Parameters controlled by lubricant additive function (Figure 28) are optimised in the development process to meet the performance requirements of the engine. Results of these designs (Table 5) have consistently enhanced system performance with higher power output. Lubricant additive development has permitted extended oil drain service intervals, enhanced fuel efficiency and improved engine durability. These factors have contributed measurably to conserving petroleum and other natural resources.

The contribution that lubricant additives have made in the above areas may most effectively be illustrated by considering the concept of Stress on the Lubricant. This is expressed as engine Power per quantity of oil used per unit of distance travelled. The quantity of oil used must take into account both oil changes and top-up. Figure 27 shows this graphically using the data from Table 5. The capability to absorb a sixty fold increase in stress over a period of just over fifty years is almost solely attributable to additive technology.

Exhaust emissions

Vehicle and engine system designs have to meet increasingly stringent exhaust emission standards, Figure 29. 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[21]. 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.

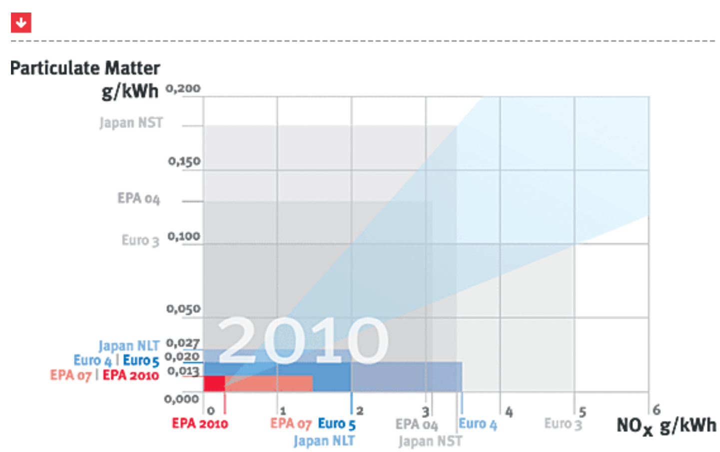


Figure 29. Global emissions standards for Heavy Duty vehicles (Source: Purem)

Health, Safety and the Environment

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 providing nomenclature on additives, disclosure of appropriate detail on composition and hazard information and producing best practice guidelines for specific substances[22].

Historically, additive manufacturers have collaborated in the testing of major additive classes. A recent example of this was the voluntary participation in national and international chemical initiatives (e.g. US EPA High Product Volume; ICCA SIDS) to generate data on a significant number of chemical classes, covering the main additive families included in crankcase lubricants.

The majority of lubricant additives are of low mammalian toxicity[2] and are typically less harmful when ingested than familiar household products. Some lubricant additives are suspected of being harmful to aquatic organisms and most show a degree of persistence but 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[23]. Additive suppliers provide this information to downstream users through hazard communication documents such as the Safety Data Sheet (SDS) and product label, which contain relevant instructions for safe storage, use and disposal.

The composition of the crankcase lubricant changes during use. Some additives are chemically changed or even destroyed 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.

The fate of the lubricant additive portion of these products is discussed in more detail below.

Lubricant additives - user benefits

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.

EUROPEAN CRANKCASE LUBRICANT ADDITIVE INDUSTRY PROFILE

This section discusses the size and nature of the crankcase lubricant additives business in Europe, examines the end use of additives and provides the basis to consider their fate and environmental impact.

The scope of this review is limited to products used in four-stroke internal combustion engines in road vehicles, which represents most of the crankcase additive use in Europe. Other markets including agricultural, railway, off-highway construction, two stroke engines and stationary engines are less well defined and are excluded.

Sources of data

No public data sources give a comprehensive guide to the size of the crankcase additives market in Europe. Market information is available from consultants for a fee[24,25]. Estimates of the market size are also held by individual ATC member companies, but these are confidential.

The methodology used here has been to request those ATC members marketing complete crankcase additive packages to supply European sales data. These were sent to Cefic for analysis according to their protocols.

The information requested by ATC to be submitted to Cefic was a detailed breakdown into components of the top 80% (by volume) of additive packages sold in the EU-15 countries, for both passenger car and commercial vehicle market segments. From these data the total additive volume has been obtained, which together with the additive treat rate gives the total crankcase lubricant volume in the EU-15 countries. This total figure is divided into passenger car use - PCMO - (1,270 kilotonnes/year) and commercial vehicle (truck, bus, etc.) use - HDDO - (1,330 kilotonnes/year) and is shown in Table 6. These data are also compared with the EuropaLub study[26] of the EU-15 crankcase lubricant market.

In the previous version of this brochure, the crankcase lubricant market estimates were based on OECD Europe in 1990. Since then the OECD has expanded membership and no longer forms the best basis for comparisons. However, to make a link back, the EU-15 data have been expanded to include the 1990 OECD members. This is also shown in Table 6.

Estimated crankcase lubricant market (kilotonnes) based on:	Passenger Car Motor Oils	Commercial vehicle engine oils	Total
ATC member data (2005 – EU-15)	1270	1330	2600
EuropaLub report (2004 – EU-15)	913	744	1657
EuropaLub report (2004 – OECD-93)	973	902	1875
ATC Document 49 (1993 – OECD-93)	1200	1400	2600

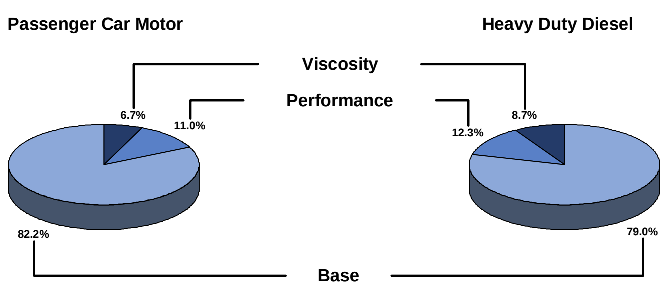
Table 6. Estimated crankcase lubricant market

As can be seen there is a discrepancy between the routes. Estimating the EU-15 crankcase lubricant market based on additive sales leads to a higher estimate, 2,600 kilotonnes, than the lubricant market based on the EuropaLub report, 1,657 kilotonnes. The EuropaLub report is based on lubricant sales in these countries. This ignores additives produced in the EU-15 and exported for blending elsewhere, and also finished lubricant exports. Both of these routes are included in the estimate based on additive sales, which as expected is a higher figure.

Despite constant additive volumes sold in Europe, the EuropaLub data do clearly reflect that finished lubricant volumes in Europe are declining, a trend that has been visible for a number of years. Comparing the OECD market data from 1990 given in the earlier publication of Document 49[27] with the 2004 EuropaLub data shows an annual decline of 2.3% of the European lubricant market. Since the lubricant market is generally aligned with growth of the GDP the actual decline is even larger. This decline is largely attributed to decreases in oil consumption rates and increased oil drain intervals.

It is also interesting to note that the passenger car market has decreased less rapidly than the commercial vehicle market. This is attributed to the lesser emphasis on drain intervals in passenger cars than in commercial vehicles where operating costs are a greater concern.

Weighted average typical finished lubricants have been established for the two categories. The lubricants are split first into their main component categories - base stock, viscosity modifier, and performance package, Figure 30. The viscosity modifier and performance packages are then further split into their major constituent additive components, Figure 31. Simple calculations using the crankcase oil tonnages in Table 6 and the formulations in Figure 30 and Figure 31 give us tonnages for the principal additive components (Table 7).



Viscosity modifier consists of varying proportions of polyhydrocarbon and polymethacrylate types

Figure 30. Finished crankcase lubricant formulations

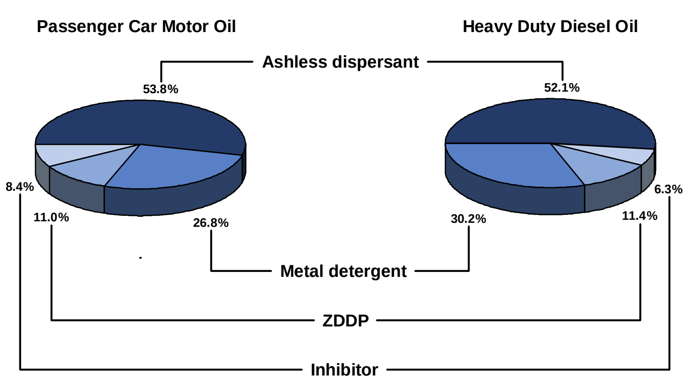


Figure 31. Additive package formulations

Market for crankcase additive components Calculated from weighted average typical lubricant composition OECD Europe (kilotonnes)			
Additive component	**PCMO**	**HDDO**	**Total**
Performance Package			
Ashless dispersant	64.7	72.4	137.1
Metal detergent	32.1	42.0	74.1
ZDDP	13.2	15.8	29.0
Inhibitor	10.1	8.8	18.9
Sub-Total Performance Package	**120.2**	**139.0**	**259.1**
Viscosity Modifiers			
VM	70.8	95.5	166.3
D-VM	2.6	1.9	4.5
Sub-Total Viscosity Modifiers	**73.4**	**97.4**	**170.8**
Total	**193.6**	**236.4**	**430.0**

Table 7. Market for crankcase additive components

Typical performance additive packages

The concept of the typical package is a major assumption. Hundreds of different additive packages are on the market - all confidential to the supplier. However, it is considered that for present purposes, bearing in mind the accuracy of other data, the typical package concept is both useful and appropriate. 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. The current data are comparable to the 1993 data by adding the calcium and magnesium detergent values in the latter.

Comparing the data in Figure 31 to the 1993 data shows some interesting trends such as the decrease in metal detergents – most visibly in commercial vehicle lubricants – due to lower fuel sulphur levels require less base reserve. Also a decline in ZDDP levels are seen which reflects the concerns on the impact of phosphorus on exhaust gas after-treatment systems.

Viscosity Modifiers

Although there are different types of viscosity modifiers they have been combined for this purpose. Occasionally they are mixed with the additive package, but are more usually sold separately, with the lubricant producer choosing one or the other.

If we look at the overall lubricant composition it becomes apparent that the average treat rate has increased for both passenger car and the commercial vehicle segment. This is a reflection of the increased performance requirements and extended drain intervals: enabling longer drain requires more high performance additives.

Most crankcase lubricants are multigrade, containing viscosity modifiers. However, some monograde oils are still sold in Europe, but as the volume is small no allowance has been made for monograde oils when estimating weighted average typical viscosity modifier concentrations.

THE ULTIMATE FATE OF CRANKCASE LUBRICANT ADDITIVES

Crankcase lubricants, as identified in the previous section are here followed through to their ultimate fate in the air, water or soil compartments. ATC member companies seek to ensure proper use of their products, to develop further knowledge of the related environmental processes, and to ensure that appropriate information is available. Other industry partners have placed increasing emphasis on the re-use and safe disposal of used oil. OEMs have given much emphasis over the last five years to the recycling of used engine oil. The re-refining of used oils has also increased.

Figure 32 traces the fate of crankcase lubricants from sale through to the environmental compartments. The environmental pathways for lubricants used in the passenger car and truck sectors are the same. Thus crankcase lubricant additives also follow these same general pathways, to their ultimate fate in the air, water or soil compartments.

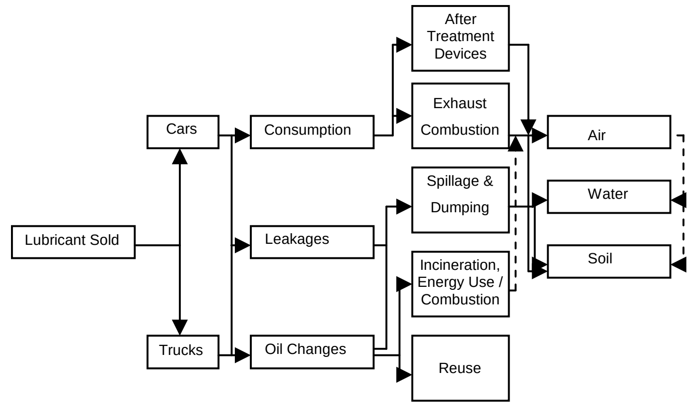


Figure 32. Flow diagram of fate of lubricants

Crankcase lubricants enter the engine when either the sump is filled or when the engine is topped up. They leave the engine

- in drained, used oil or
- as leakage through seals or gaskets during use or
- via lubricant consumption down the tailpipe as gaseous emissions (combustion products or particulates).

If the vehicle is fitted with a particulate trap, the incombustible portion of the lubricant in the exhaust will be trapped by this filter.

Broken lines in Figure 32 show that a portion of used oil which is collected and burnt or incinerated contributes to emissions in the air compartment - and that, ultimately, some emissions to the air compartment end in the soil or water compartments.

Approximately 2,600 kilotonnes of crankcase lubricants were sold in EU-15 Europe in 2005. It is estimated that 24% of lubricants sold for both passenger cars and trucks is consumed during operation[28,29]. The lubricant leaves the engine down the tailpipe as emissions of either combustion products (gases or vapour) or particulates (which will be collected if a particulate trap is fitted). A portion of the lubricant (and fuel) combustion products is entrained and re-dispersed in the crankcase lubricant itself, or forms deposits in the engine.

Leakage past seals or gaskets is estimated to be negligible for both cars and trucks. The environmental routes of this portion of the lubricant are to the water and soil compartments.

Used oil should be drained from the crankcase, collected and re-refined and re-used, or disposed of suitably. Approximately 75% of lubricants sold (2,000 kilotonnes) is drained as used oil at oil changes. This includes oil from scrap vehicles. A significant proportion (estimated 47%[30]) of that collected is used as fuel oil or incinerated for energy value or disposal. Regeneration represents an estimated 24% of the total waste oil. Additives in oils properly disposed of by these routes end up as solids for landfill, used in cement or as gaseous emissions. However, approximately 28% of used oil is still unaccounted for and may be dumped into the soil and water compartments, or burnt entering the air compartment. The proportions going to the various pathways are illustrated in Figure 33.

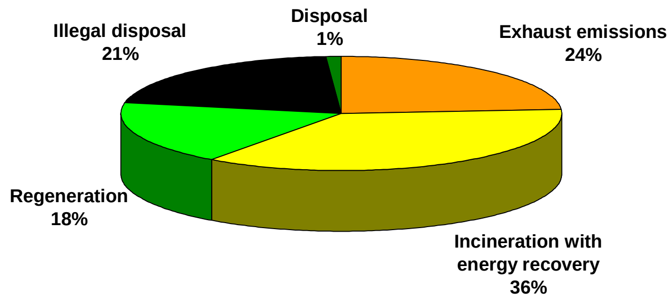


Figure 33. Fate of lubricants in Europe

A model has been established based on the above analysis and used by the ATC to estimate the proportions of crankcase lubricants and additives going into the three environmental compartments. It is shown schematically in Figure 34.

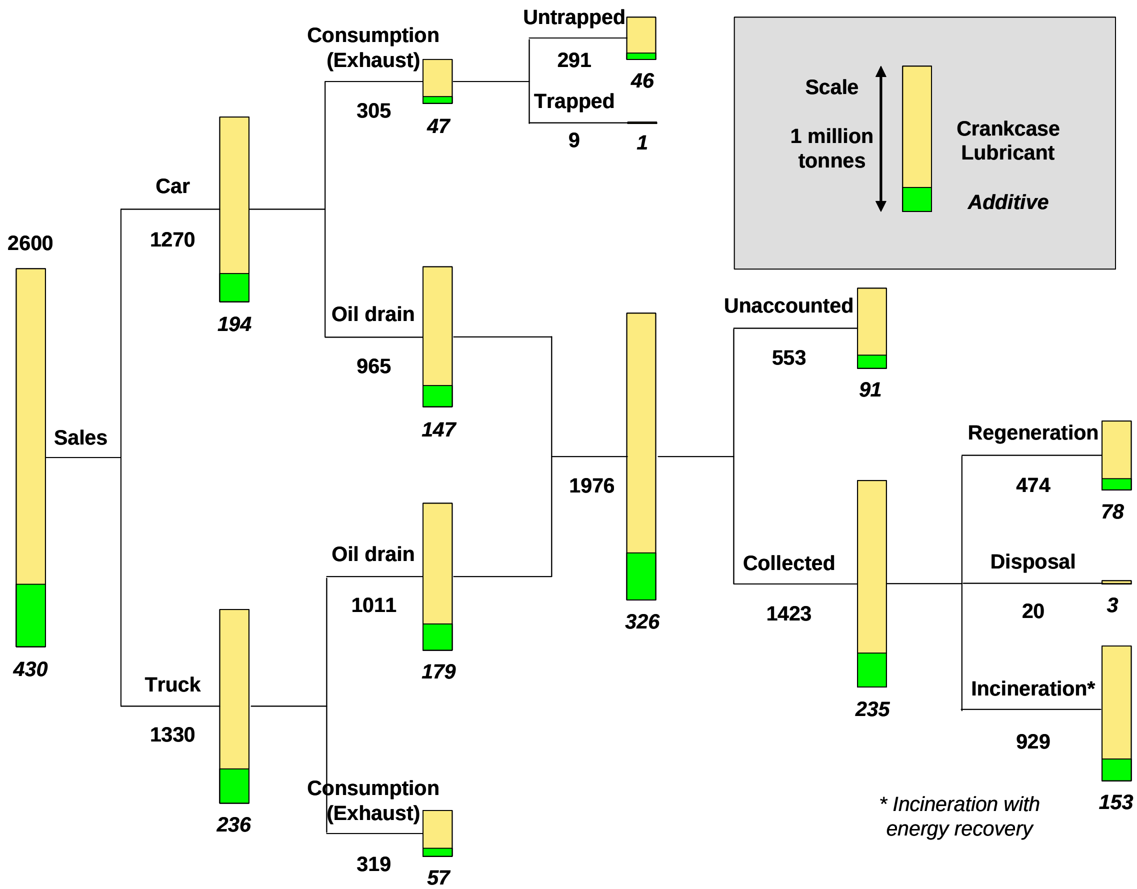


Figure 34. Fate of crankcase lubricants EU-15 2005 (figures in kilotonnes)

Re-refining/re-use

It is estimated that in OECD Europe some 475 kilotonnes a year of used crankcase lubricant is re-refined. These base stocks and then used, after appropriate treatment, in the same way as virgin base stocks. Given that the conversion process yield is typically 80%[31], some 380 kilotonnes of re-

refined basestocks are produced annually. This represents approximately 18% of the total base stocks used in crankcase lubricants. Re-refining and re-use prolongs the life of limited natural resources.

Re-refining also produces an estimated 35 kilotonnes a year of residual sludge. After appropriate treatment to neutralise it, the sludge is used in cement manufacture or road construction, or otherwise disposed of in landfills.

Incineration/use as fuel oil

It is estimated that up to 930 kilotonnes of used oil is burnt either as fuel oil or for heat recovery in incinerators. Again these activities provide significant environmental benefits - it has been estimated[32] that burning one tonne of used oil saves the use of 0.85 tonne of heavy fuel. These quantities include some 150 kilotonnes of additives, of which no more than 7.5 kilotonnes are elements other than carbon, hydrogen or oxygen, and not more than 4 kilotonnes is metallic (calcium, magnesium and zinc). Incineration is regulated in the EC and monitored throughout the member states. Emissions originating from the additive content of used oils therefore present no new or unregulated environmental hazard.

Used oil/leakage

About 550 kilotonnes a year of used oil is either unaccounted for or lost. At worst, this ends up in the water compartment, either directly or indirectly through the soil compartment. This used oil contains approximately 90 kilotonnes of additives. It should be noted that these figures have decreased by nearly 50% since the previous assessment was made in 1993.

The additives in used oil which could potentially enter the water compartment comprise mainly carbon, hydrogen and oxygen. The quantities involved do not represent a major environmental concern relative to total hydrocarbon leakages in OECD Europe. However, dumping into the environment is unnecessary and unacceptable pollution which is being addressed by stricter implementation of existing regulations, and an increased focus on collection of used oil.

The remaining elements and approximate quantities comprise calcium/magnesium (1,350 tonnes), zinc (600 tonnes), sulphur (1,600 tonnes), phosphorus (530 tonnes) and nitrogen (350 tonnes), the use and benefits of which are discussed in earlier sections. The performance of internal combustion engines could not be maintained effectively without them. Research has not yet identified alternative chemicals which offer the same benefits of reduced emissions, enhanced fuel economy and lower oil consumption, and could be considered more environmentally benign.

Exhaust emission calculations

The contributions to vehicle exhaust emissions from lubricant additives have been estimated. The key assumptions related to combustion are as follows:

- All oil and additive fractions are burnt at the same rate. This represents a worst case assumption.
- All the nitrogen in the lubricant from the additives is converted to NOx. This represents a reasonable worst case assumption.
- All the additive metals burnt during combustion contribute to particulate formation. (Also a worst case assumption for estimating the additive contribution to particulates.)
- The amount of combusted lubricant which contributes to engine deposits is insignificant compared to the total combustion products.

The first assumption that oil and additive fractions are consumed at the same rate suggests additive concentrations in drained oil are the same as in fresh. In practice, concentrations may increase or decrease, depending on engine type and operating characteristics. There are two primary modes of oil consumption - volatility and bulk loss. In hot-running engines designed for low oil consumption, the additive concentration will tend to increase within the oil drain interval, due primarily to oil volatilisation. For calculation of additive contributions to exhaust emissions, therefore, the first assumption in the model represents a worst case scenario.

With modern aftertreatment systems the NOx and particulates, both lubricant and fuel derived, will be significantly reduced.

Finished lubricant

Weighted average formulations have been derived from data supplied by ATC members as described above. The additive contents of Passenger Car Motor Oil (PCMO) and Heavy Duty Diesel Oil (HDDO) formulations are shown in Table 8. The main elemental contents in the oil arising from the additives are shown in Table 9.

Additive component	Passenger Car Motor Oil	Heavy Duty Diesel Oil
Ashless dispersant	5.9%	6.4%
Metal detergent	3.0%	3.7%
ZDDP	1.2%	1.4%
Inhibitor	0.9%	0.8%
Viscosity modifier	6.7%	8.7%
Total Additive Content	17.8%	21.0%
Base stock	82.2%	79.0%
Total	100.0%	100.0%

Table 8. Weighted-average crankcase lubricant composition, Mass percent

Contribution from additives - weighted averages (mass %)		
	Passenger Car Motor Oil	Heavy Duty Diesel Oil
Calcium & magnesium	0.24%	0.30%
Nitrogen	0.07%	0.08%
Zinc	0.11%	0.12%
Phosphorus	0.10%	0.11%
Sulphur	0.26%	0.36%
Plus other contributions to carbon, oxygen and hydrogen contents		

Table 9. Elemental content of crankcase oils

Fuel consumption

The amount of fuel used is based on quoted oil industry, EC and national government statistics[15] (Table 10). For passenger cars, fuel consumption in L/l00 km is based on quoted vehicle fuel economy figures. For trucks, the fuel consumption in g/kW.h is the weighted average for different vehicle types and populations.

Fuel Consumption OECD Europe 1998[15]		
	Gasoline	Diesel
Annual fuel consumption million tonnes	127	130
Average per vehicle	Cars 7 L/100km	Cars 7L/100km Trucks 180g/kW.h

Table 10. Fuel consumption

Fate - by element

Table 9 shows the percentage of main elements originating from additives for the weighted average PCMO and HDDO formulations. The greatest proportion is carbon. Other elements comprise no more than 1% of the total lubricant. The fate of these elements will each be dealt with in turn. Because of the experimental difficulty in segregating the contributions of all the elements in the combustion process, some further details of the average assumptions are given below.

Fate of carbon

When fuel is burnt in cars and trucks, most of the carbon forms carbon dioxide (Table 11[31]). Small proportions end up in particulates and partially burnt hydrocarbon fractions. Data shown in table 11 are for engine out emissions. Aftertreatment devices will remove particulates and convert hydrocarbons and carbon monoxide to carbon dioxide (and water). Carbonaceous particulate matter will also be converted to carbon dioxide during the regeneration phase.

	Particulates	CO_2	CO	HC
Cars	0.1	88.0	11.2	0.7
Trucks	0.3	99.0	0.6	0.1
Source: Volkswagen[33]				

Table 11. Fate of fuel carbon during combustion

On the basis of ATC and industry statistics[15,33], the following assumptions are used in the model calculations: 20% of the carbon from the lubricant consumed in trucks contributes to particulates, 20% goes to CO, 20% to hydrocarbons, 5% remains suspended in the oil and the remainder is burnt to CO_2. A similar judgement for gasoline powered cars suggests that 5% of the carbon from the lubricant consumed contributes to particulates, 5% goes to CO, 5% to hydrocarbons, 1% remains in the oil and the remainder is burnt to CO_2.

Similarly, in proportion, additive carbon contributes to the engine out emissions of carbon monoxide, unburnt hydrocarbons and particulates, and carbon dioxide. These will be modified as above by the aftertreatment system.

Fate of nitrogen

The model contains the assumption that all combusted additive nitrogen forms NOx in the combustion chamber. Due to the relatively low level of nitrogen in lubricants (Table 9) there are no firm experimental data to support this assumption but, as a reasonable worst case, additive nitrogen can be also considered as a contributor to engine out NOx emissions. However since the introduction of the Euro IV emissions legislation, exhaust emissions of NOx from all sources have been significantly reduced.

Other elements

It is assumed that all the additive metals burnt during combustion contribute to particulate formation. Magnesium and calcium form sulphates, whilst zinc goes to both zinc oxide and zinc pyrophosphate. The emissions of lubricant derived metals (S, Ca, Zn, P, and Mg) are highly correlated with emissions predicted from the composition of oil (and fuel sulphur); however, recovery rates vary considerably (ranging from 17% for Mg to 125% for S)[34].

Comparison with legislative limits

Light duty

EC regulated emission levels for passenger cars have been significantly reduced over recent years, and are now greatly reduced compared with those in place when this document was first issued. However, the contribution from lubricant additives to these regulated emissions levels (Table 12) remains small, at about 0.1% for hydrocarbons plus NOx and 0.2% for CO of the regulated emissions level taking worst case assumptions based on engine out emissions. However lubricant additives, together with engine design improvements, have permitted successive reductions in regulated emissions.

Estimated emissions EU-15 2005		
	Kilotonnes	**g/km**
CO_2	109	0.04
HC	2.1	0.001
NOx	0.45	
CO	4.1	0.002
Comparison with current/future EC legislation g/km (gasoline/diesel)		
	Euro 4	**Euro 5**
HC + NOx	0.18/0.30	0.16/0.23
CO	1.0/0.5	1.0/0.5

Table 12. Light duty engine exhaust emissions

Heavy duty

Heavy duty diesel emission limits have also been considerably reduced within the EC over the years, with further reductions planned in 2009. Once again, the additive contribution (Table 13) to regulated emission levels of CO, NOx and hydrocarbons can be considered small.

Because fuel derived particulates have been reduced to a very low level, additives now make a relatively more significant contribution to particulate emissions. As limits have been reduced, up to 50% of the regulated particulate weight may originate from lubricant additives. It must be emphasised again that the assumptions made to calculate the additive contribution represent the absolute worst case.

Estimated additive-derived emissions EU-15 2005		
	Kilotonnes	g/kW.h
Particulates	7.1	0.01
CO_2	45	0.07
HC	8.3	0.01
CO	16.5	0.03
NOx	0.51	0.001
Comparison with current/future limit values g/kW.h		
	Euro IV	Euro V
Particulates	0.02	0.02
HC	0.46	0.46
CO	1.5	1.5
NOx	3.5	2.0

Table 13. Diesel engine exhaust emissions

These contributions to particulate emissions must be seen in the context of a considerable net environmental gain. Use of additives has enabled regulated particulate emissions to be reduced to the current low level of 0.02g/kW.h. This has been achieved by engine technology which would not have been possible without additives which, at worst, will-contribute just 0.01g/kW.h to particulate emissions. The total contribution due to additives of some 7,000 tonnes over the whole of EU-15 is relatively small. Engine and aftertreatment manufacturers together with the lubricant and additive industry continue research to reduce further these emissions.

These contributions must be compared with the environmental benefits that the use of additives has brought in terms of reduced emissions and lower fuel and oil consumption.

Contribution to unregulated emissions

Carbon Dioxide

Carbon dioxide, whilst not technically a regulated automotive emission, is of great concern as the EU examines ways to meet its Kyoto Agreement commitments. Approximately 750 million tonnes of CO_2 is emitted-each year from the automotive use of gasoline and diesel fuels in OECD Europe. Of this, it is estimated that one million tonnes is derived from the lubricant and even less (approximately 160 kilotonnes) from the lubricant additives. Balanced against this small contribution are significant reductions in CO_2 emissions from improvements in fuel economy achieved from additive-based finished lubricants. Earlier analysis showed that the combined impact of fuel-efficiency in engine, lubricant and additive design over the twenty years to 1990 resulted in an annual reduction in CO_2 emissions from transport by over 100 million tonnes a year in OECD Europe (1990)[29]. This trend continues, as illustrated in Figure 26.

Chlorine

Regulators and environmental protection organisations have expressed concern about the chlorine content of all chemical products because of the potential to create dioxins when combusted. Crankcase lubricant additives marketed by ATC member companies do not contain chlorine as a deliberately introduced functional component. Some important classes of additive components contain traces of chlorine as a by product of manufacturing processes: namely some detergents, ashless dispersants and other ashless products. However, recent studies[35,36,37,38] have shown that the trace amounts of chlorine in commercial engine lubricants do not contribute to vehicle dioxin and furan emissions, within the detection limits and test capabilities currently available.

Phosphorus

The most common source of phosphorus is zinc dialkyldithiophosphate (ZDDP). Typical concentrations in lubricants are shown in Table 9 and Table 10. In response to concerns about the impact of phosphorus on catalytic aftertreatment systems, phosphorus levels in lubricants have been significantly reduced over the last decade.

SUMMARY AND CONCLUSIONS

This paper is an update from the 1993 edition and describes the function and chemistry of the additives used in automotive crankcase lubricants for passenger cars and trucks. The benefits provided by these additives are identified and the fate of the additives in the environment is analysed.

The additive industry continues to invest more than €100 million each year in technology development aimed at improved protection of automotive crankcase and aftertreatment systems.

European market size – EU15, 2005

The European crankcase lubricants market in 2005 was estimated at 2,600 kilotonnes split between passenger cars (1,270 kilotonnes) and commercial vehicles (1,330 kilotonnes). This amount is approximately 1% of fuel sold.

Lubricant additive EU15 sales data from 2005 supplied by the major additive marketers have been used to estimate the European lubricant additive market and to calculate typical weighted average finished lubricant compositions of both passenger car and commercial vehicle engine oils.

The lubricant additives market is approximately 430 kilotonnes - 194 kilotonnes passenger car lubricants and 236 kilotonnes commercial vehicle lubricants.

Fate analysis

A fate analysis of lubricants and lubricant additives has been carried out for both passenger car and commercial vehicle lubricants. Crankcase lubricants are used to fill the vehicle sump at the recommended service interval, and for top-up in between. Lubricants leave the engine through lubricant consumption; down the tailpipe as gaseous emissions (combustion products or particulates), leakage through seals and gaskets during use, or in drained used oil at oil changes. Increasingly particulate traps are being fitted to vehicles which also capture ash derived from the lubricant.

For Europe, figures derived from the analysis are as follows:

- Ratio of fuel to oil burnt - 410:1
- 75% (326 kilotonnes) remain in the drained used oil
- 24% (104 kilotonnes) is emitted in the vehicle exhaust together with fuel combustion products
- The amount lost to spills and leaks is negligible

Fate of Additives – Air compartment

Regulated emissions

Lubricant additives contribute less than 1% of both the Euro IV regulated limits and the Euro V proposed limits for CO, NOx and HC emissions.

Lubricant additives can contribute up to approximately 50% of the permitted particulates emissions. Research continues to reduce particulate emissions, through development of low ash lubricants and through the use of particulate filters.

Carbon Dioxide CO_2

Crankcase lubricant and lubricant additive combustion contributes little to the greenhouse gas, carbon dioxide, in comparison to total CO_2 emissions in EU-15 of 3,506 million tonnes in 2006[39]. Of this, 23% or 806 million ton CO_2 is attributed to road transport[40] (ref. 2). This means that the 0.15 million tons CO_2 attributed to crankcase additives is approximately 0.02% of the total CO_2 emission from road transport.

Fate of additives – Drained used oil

Re-refining/reuse

Industry and government data on the use and fate of used oils are incomplete. It is estimated that 75% (c. 2,000 kilotonnes) of all crankcase oil sold, is drained. Of this it is estimated that a quarter, 500 kilotonnes, is re-refined producing lubricant basestock. It is estimated that 1,000 kilotonnes of used crankcase oil is burnt, saving approximately 0.85 tonne of heavy fuel oil for each tonne of used oil burnt.

Fate of additives - water and soil compartments

Calculations suggest that approximately 730 kilotonnes of used crankcase oil (containing 120 kilotonnes additives) is unaccounted for and could enter the water and soil compartments. Unauthorised dumping may account for much of this.

Crankcase lubricant additives undergo chemical change during use. Used oil contains compounds of calcium, magnesium, zinc and phosphorus in addition to carbon, hydrogen, nitrogen and oxygen. Trace amounts of chlorine compounds do not contribute to dioxin and furan emissions.

Improvements to the practices in reuse or disposal of used oils would reduce environmental impact.

Benefits

Crankcase lubricant additives provide significant benefits to both the environment and the consumer. These include enhancing engine durability, cleanliness and friction reduction, maintaining low exhaust emission levels and optimal fuel economy for the vehicle. Recent lubricant development has focussed on ensuring compatibility with exhaust aftertreatment systems.

Lubricant additive technology enhances performance of base fluids derived from a variety of crude oils. These lubricants can then be used with a wide variety of fuels derived from different crude oils and processes. Optimum use of petroleum resources is thus achieved.

Development of lubricant additive technology is costly, requiring extensive engine testing and field evaluations. The additive industry spends €115 million annually in Europe on new developments. Lubricant additives are engine design components, enabling the continuing evolution of engine design to provide increasingly efficient and more environmentally-friendly vehicles. Lubricant additives provide high performance engineering for the consumer and ensure reliability, longevity and optimal performance of the vehicle.

Lubricant additives, as a class, are low environmental risk chemicals and the ATC is committed to ongoing health and safety reviews.

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