R.M. Mortier
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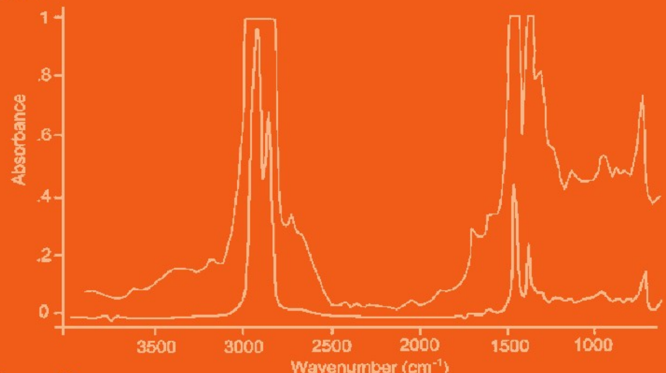
Chemistry and Technology of Lubricants

3rd Edition



Springer

Chemistry and Technology of Lubricants

Roy M. Mortier · Malcolm F. Fox ·
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Editors

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Third Edition

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Preface

The third edition of this book reflects how the chemistry and technology of lubricants have developed since the first edition was published in 1992. Refinery processes have become more precise in defining the physical and chemical properties of higher quality mineral base oils, Part I, Chapters 1 and 2, beneficial with the move away from Gp.I mineral base oils towards Gps.II and III, synthetic base oils such as poly-α-olefins (PAOs), the esters and others. New and existing additives have improved performance through enhanced understanding of their action, Part II, Chapters 3–7. Applications have become more rigorous, Part III, Chapters 8–14. The performance, specification and testing of lubricants has become more focused on higher level requirements, Part IV, Chapters 15–17. The acceleration of performance development in the past 35 years has been as significant as in the previous century. The performance and life between service changes of lubricants have extended dramatically and are expected to extend more, Chapters 9 and 10. Yet more performance will still be required but it will also include the lubricant's ability to 'stay in grade' for efficiency savings and withstand the conditions arising from the use of advanced environmental emission controls, such as for Euro 5 and 6 engines and their North American equivalents.

The physical benefits of having a lubricant film between surfaces in relative motion have been known for several millennia. Dowson [1] found an Egyptian hieroglyph of a large stone block hauled by many slaves. Close inspection shows fluid, presumably water, being poured into the immediate path of the block. Moderately refined vegetable oils and fats were increasingly used to lubricate machines and carriage/wagon bearings; the benefits of reducing the force needed to operate them were a widely received wisdom up to the end of the middle ages, $\sim$1450 AD. Increasing industrialisation after 1600 AD, accelerated during the First Industrial Revolution in Britain after 1760 AD, soon followed by other developed countries, recognised the important contribution that lubricants made in reducing the work required to overcome friction and in extending the working life of machines. The crude technology existed and was effective for its time but it was not understood.

Leonado da Vinci was the first person recorded to investigate the resistance to motion of two 'smooth' loaded bodies in contact. He set out the Laws of Friction as we now essentially know them [2] but they were not appreciated and nor applied at the time. Whilst Amontons in 1699 [3] and Coulomb in 1785 [4] essentially re-discovered and extended the Laws of Friction, they concentrated on lubricant effects at the surfaces of two contacting blocks of material in relative motion. They recognised that the surfaces were rough, on a fine scale, and suggested that lubricants held in the crevices and recesses of those surfaces reduced their effective roughness. This concept explained the effects of lubricants for the relatively unsophisticated technology up to the 1850s.

Increased power densities and throughputs placed greater attention upon the lubrication of bearings and both Tower [5] and Petrov [6] separately showed in 1883 that a shaft rotating in a lubricated bearing has a full, coherent film separating the two components. The fluid film thickness was many times that of the surface roughness dimension. Reynolds [7] studied the viscous flow of lubricants in plain bearings in 1886 and his analysis of the results led to the differential equation of pressure within contacts, Eq. (1), that continues as the basis of full fluid film lubrication – hydrodynamic lubrication.

$$\frac{dp}{dx} = 6\eta \left(U_o + U_h\right) \left[\frac{h - h_m}{h^3}\right] \tag{1}$$

Equation 1 is an integrated Reynolds equation for the hydrodynamic lubrication of a bearing (for steady state one-dimensional relative motion flow with negligible side leakage (transverse flow) where p is fluid pressure, x the one-dimensional distance into the bearing, h the film thickness and h_{m} at maximum pressure).

But hydrodynamic lubrication does not always apply. Hardy [8] identified the separate condition of low relative speeds, high loads and low-lubricant viscosities in 1922. Under these conditions the fluid film is not coherent because of the combination of high load and low viscosity and the surfaces are in contact at the tips of the surface roughness, the asperities. In a memorable analogy, Bowden and Tabor [9] described two surfaces in contact as ‘Switzerland inverted upon Austria, with only the mountain peaks in contact’. Deformation of the peaks in contact under load and surface films formed from the lubricant fluid and its constituents determine the friction and wear of these contacting surfaces. Understanding the role of surface films recognised a new mechanism, that of boundary lubrication, separate from hydrodynamic lubrication. Types of additives were developed to modify surface films, either by surface absorption or reaction at the interface, to dramatically reduce friction and wear from the 1950s onwards. Understanding the mechanisms of additive action has been aided by surface analyses and informed molecular synthesis.

Dowson and Higginson [10] completed the range of lubrication mechanisms by demonstrating that under extreme loading between contacts, such as in a rolling element bearing between the roller or ball and its cage, the very high pressures generated within the contact caused a plastic deformation of the contact materials together with a pressure-induced enhanced viscosity of the lubricant. This is elastohydrodynamic lubrication, or EHL, which has been of immense value in understanding and predicting the behaviour of thin films in highly loaded contacts. The relationship of these forms of lubrication is shown in the well-known curve brought together by Stribeck [11] (Fig. 1).

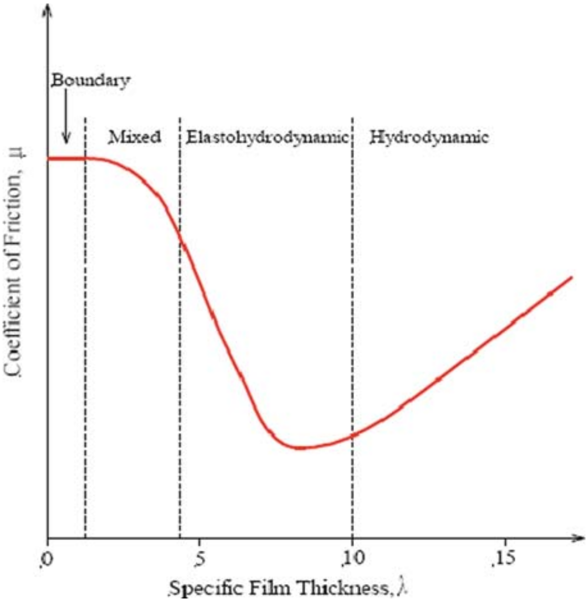

Fig. 1 The Stribeck curve

Lubricants are a component part of a mechanical system and must be developed in parallel with that system, as is seen in the API and ACEA specifications, Chapter 17. When that axiom is not followed, then wear and reliability problems begin to occur as extensive wear and serious machine damage. Thus, steam engines in the 1870s were developing to higher power densities through increased steam temperatures and pressures. ‘Superheating’ of steam removed liquid droplets to produce a homogenous, working fluid at higher temperatures. The natural fats and oils used as lubricants of the time began to break down under the enhanced physical working conditions and their degradation products, particularly the organic acids, corroded steel and particularly non-ferrous metal components. The performance demands of the system had moved ahead of the ability of the lubricants to perform and protect it. Fortunately, just at that time, heavier hydrocarbons from crude petroleum production began to be available for use as lubricants which were able to withstand higher temperatures in high-pressure steam environments.

The initial main driving force for the development of the oil industry in the latter half of the 19th century was the supply of lighting, or lamp, oil to augment and then replace animal and vegetable lamp oils. Mineral oil seepages from many natural surface sites had used the lighter components as lamp oils with the heavier components as lubricants and the heaviest components as pitch for caulking and waterproofing. As demand built up for liquid hydrocarbon fuels into the 1920s, the heavier hydrocarbon lubricants became much more readily available for heavy machinery and automotive use. In retrospect, the internal combustion engines of the time had low energy densities and did not stress the simple base oils used as lubricants.

This relatively unchallenged situation was upset in the mid-1930s by Caterpillar introducing new designs of higher power and efficiency engines for their tractors and construction equipment [11]. These characteristically rugged engines were very successful but soon developed problems due to extensive piston deposits resulting from degradation of the lubricants available at that time. Piston rings, stuck in their grooves by adherent carbonaceous deposits, lost their sealing action and engine efficiency declined. Caterpillar responded by developing a lubricant additive to remove and reduce the adherent carbonaceous piston deposits, the first 'additive' as would be recognised now. Whilst successful, variable results were found in the field for different base oils and Caterpillar developed a standard test for the effectiveness of lubricants. This is a classic case of machine system development moving ahead of lubricant performance. However, two major developments can be traced from it, first, the additive industry and second, the system of specification and testing of lubricants as now organised by API, ACEA and ILSAC, Chapter 17.

A further step change required for lubricant performance came from the development of the gas turbine in the 1940s. New lubricants were needed to withstand higher operating and lower starting temperatures, for conventional oxidation of unprotected mineral hydrocarbon oils accelerates above 100°C yet their flowpoints are limited to –20°C or so. Synthetic base oils, either as esters derived by reaction from vegetable sources or as synthetic polymers, have been developed initially for the aircraft industry, then aerospace, with wider liquid ranges and superior resistance to thermal and oxidative degradation (Chapter 11 and 12). Their superior performance has now extended into automotive and industrial machinery lubricant formulations.

The reality of machine operation, of whatever form, is related to the regions of the Stribeck curve, Chapter 8. When a machine is operating, with solid surfaces sliding, rotating or reciprocating against each other, then a fluid film of lubricant separates them as the physical effect of hydrodynamic lubrication. A general trend driven by increased efficiencies has increased bearing pressures and reduced lubricant fluid viscosity, giving thinner mean effective film thicknesses. Dowson [12] has demonstrated the thicknesses of fluid film under hydrodynamic and elastohydrodynamic conditions relative to a human hair diameter (Fig. 2).

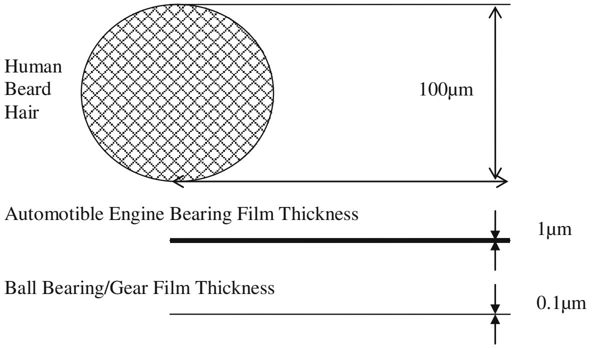

Fig. 2 Relative lubricant film thicknesses (after Dowson [12])

The problem with thin fluid film lubrication occurs when the relative motion of the solid surfaces either stops completely, stops at reversal in reciprocating motion or the dynamic loading of a cam on its follower, one gear tooth on another or on a journal within a bearing such that this lubrication mechanism fails and the surfaces make contact. Under boundary lubrication conditions the role of adsorbed molecular films of protective additives is crucial in protecting against wear.

Anti-wear additives are but one of a number of additive types formulated into base oils – there are also anti-oxidants, Chapter 4, and anti-acid, detergents anddispersants, Chapter 7, lubricity, anti-wear, extreme pressure, pour point depressants, anti-rust and anti-foam additives, Chapter 6. Viscosity index improvers, VIIs, are high-molecular weight polymers which alter the temperature dependence of the base oil viscosity, Chapter 5. Taken altogether, the additive mass percentage of a formulated lubricant can be as high as 15–20%, a veritable ‘chemical soup’ but one which is very carefully formulated and tested. The additives are often multi-functional, thus some VII compounds have a pour point depressant function, Chapters 5 and 6. Some anti-oxidants have anti-wear and also anti-acid functionality, Chapters 4, 6 and 3. Given these cross-interactions, formulation of a final lubricant product is a complex and skilled activity, Chapters 8–13.

Whilst most formulation development work has gone into vehicle automotive lubrication, Chapters 9 and 10, more specialised development has gone to formulate lubricants for specific applications such as gas turbine, Chapter 11, and aerospace lubricants, Chapter 12, the different requirements to cover the marine diesel engine size and power range, Chapter 13, industrial machinery and metal working (both cutting and forming), Chapter 8. The apparently simple, but complex in detail, formulation, manufacturing and performance applications of grease are discussed in Chapter 14.

The environmental implications of lubricant production, use and disposal are discussed in Chapter 15 to show that lubricants have an outstanding environmental record in both extending the use of hydrocarbon resources by longer service intervals and also by extending the life and reliability of machines. However, the requirements to recycle used lubricants will increase. Ensuring the reliability of machines is discussed as ‘Condition Monitoring’ in Chapter 16 and ensuring the fitness for purpose of lubricants is the subject of Chapter 17, ‘The Specification and Testing of Lubricants’.

Looking to the future, it is self-evident that further demands will be made for improved lubricant performance. The service change lifetime of automotive engine lubricants will continue to increase, whereas powertrain lubricants are already close to ‘fill for life’. The limit for engine lubricant service life will possibly be set by other constraints such as the need for annual or biennial vehicle services for all vehicle systems. Thus, North America could readily adjust its lubricant change periods over time to those already used in Europe and save many Mt/base oil each year. Problems to deal with on the way to enhanced service intervals include the effects of bio-fuels on lubricants and their performance, maintaining efficiency gains across the service life of a lubricant charge and the effects of engine modifications for even lower emissions.

To meet enhanced lubricant performance and service interval life, base oils are already moving upwards, away from Gp.I towards the more highly treated and refined mineral base oils of Gps.II and III and also the synthetic base oils of PAOs and esters. Their relative costs and benefits will determine the base oil mix, Chapters 1 and 2.

Additives have two apparent counteracting pressures. The demands for improved lubricant performance can mean more sophisticated additives, Chapters 3–7, in more complex formulations, Chapters 8–14. On the other hand, there is the pressure of the 'REACH' chemicals assessment program in the EU, paralleled elsewhere by a general direction to reduce chemical eco-toxicity on consumer products, for no business wishes to have warning cryptograms of dead fish and dying trees on its products! To meet these requirements, the 'CHON' philosophy for additives is being explored, where lubricant additives will only contain carbon, hydrogen, oxygen and nitrogen. This excludes metals such as zinc and molybdenum and the non-metals sulphur and phosphorus because of their environmental effects.This will be a stringent test of research and development.

Finally, at the end of their useful life, lubricants will be regarded as a valuable resource and re-refined/recycled into new lubricant products and fuels. Acceptance of recycled base stocks into new lubricant formulations will take time and require rigorous quality testing but will, and must, inevitably happen.

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Part I
Base Oils

Chapter 1
Base Oils from Petroleum

R.J. Prince

Abstract The source, composition and suitability of crude oils for base oil production are reviewed. The physical and chemical properties of alkanes, naphthenes and aromatics and their characteristics for lubricant applications are examined. Properties and applications of various base oils are defined and specified. Production of conventional mineral oils is described, including the various processes to remove wax and other deleterious substances, followed by increasingly severe hydrogenation to produce base oils of increased quality and performance. The API categorization of mineral base oils, either direct from the refinery or after hydrotreatment of increasing severity, is described, together with sub-categories.

1.1 Introduction

Modern lubricants are formulated from a range of base fluids and chemical additives. The base fluid has several functions but it is primarily the lubricant which provides the fluid layer to separate moving surfaces. It also removes heat and wear particles whilst minimizing friction. Many properties of the lubricant are enhanced or created by the addition of special chemical additives to the base fluid, as described in later chapters. For example, stability to oxidation and degradation in an engine oil is improved by the addition of antioxidants whilst extreme pressure, EP, anti-wear properties needed in gear lubrication are created by the addition of special additives. The base fluid acts as the carrier for these additives and therefore must be able to maintain them in solution under all normal working conditions.

The majority of lubricant base fluids are produced by refining crude oil. Estimates of the total worldwide demand for petroleum base oils were 35 Mt in 1990 and this has remained approximately stable since [1]. The reasons for the predominance of refined petroleum base oils are simple and obvious – performance, availability and price. Large-scale oil refining operations produce base oils with excellent performance in modern lubricant formulations at economic prices. Non-petroleum base fluids are used where special properties are necessary, where petroleum base oils are in short supply or where substitution by natural products is practicable or desirable.

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This chapter is concerned with base oils from crude petroleum oil. Crude oil is an extremely complex mixture of organic chemicals ranging in molecular size from simple gases such as methane to very high molecular weight asphaltic components. Only some of these crude oil constituents are desirable in a lubricant base fluid and a series of physical refining steps separate the good from the bad. Other process steps involving chemical reactions are also used to enhance properties of the oil fractions. Different types of base oils are produced at refineries with different viscosities or chemical properties, as needed for different applications.

1.2 Base Oil Composition

Crude oil results from physical and chemical processes acting over many million years on the buried remains of plants and animals. Although crude oil is usually formed in fine-grained source rocks, it can migrate into more permeable reservoir rocks and large accumulations of petroleum, the oilfields, are accessed by drilling. Each oilfield produces a different crude oil which varies in chemical composition and physical properties. Some crude oils, ‘crudes’, have a low sulphur content and flow easily, whereas others may contain wax and flow only when heated, yet others contain very large amounts of very high molecular weight asphalt, Table 1.1. Despite the wide range of hydrocarbons and other organic molecules found in crude oils, the main differences between crudes are not the types of molecules but rather the relative amounts of each type that occur in each crude oil source.

Table 1.1 Variation in crude oil properties between sources

Source	North Sea	Indonesia	Venezuela	Middle East
Sulphur content (%)	0.3	0.2	5.5	2.5
Pour point (°C)	–3	39	9	–15
Viscosity at 40°C (cSt)	4	12	19,000	8

1.2.1 Components of Crude Oil

The components of crude oil can be classified into a few broad categories. Some of these components have properties desirable in a lubricant whilst others have properties which are detrimental.

Hydrocarbons: Hydrocarbons (organic compounds composed exclusively of carbon and hydrogen) predominate in all crude oils and can be further subdivided into the following:

- *alkanes,* known as paraffins, with saturated linear or branched-chain structures,
- *alkenes,* known as olefins, unsaturated molecules, but comparatively rare in crude oils. Certain refining processes produce large amounts of alkenes by cracking or dehydrogenation,

- *alicyclics,* known as naphthenes, are saturated cyclic structures based on five- and six-membered rings,
- *aromatics,* cyclic structures with conjugated double bonds, mainly based on the six-membered benzene ring.

This is a simplified classification because many hydrocarbons can be combinations of these classes, e.g. alkyl-substituted cyclic or mixed polycyclics containing both aromatic and fully saturated rings; examples are shown in Fig. 1.1

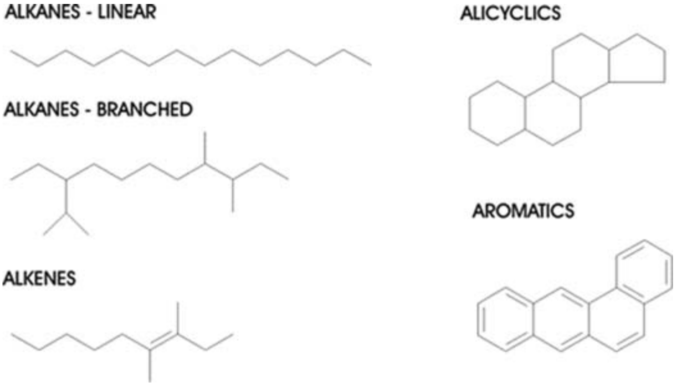

Fig. 1.1 Examples of straight- and branched-chain aliphatic, alkenes, alicyclic and aromatic hydrocarbon structures

Non-hydrocarbons: Many organic compounds in crude oil incorporate other elements, sometimes within ring structures or as functional groups attached to a hydrocarbon structure. Organosulphur compounds are generally much more prevalent than nitrogen- or oxygen-containing molecules, whilst organometallics are usually present as trace compounds. Within the boiling range appropriate to lubricant base oils, almost all organosulphur and organonitrogen compounds are heterocyclic molecules, see Fig. 1.2 for examples. In contrast, the principal oxygen-containing molecules are carboxylic acids as either saturated aliphatic acids or cycloalkanoic acids (naphthenic acids). Traces of phenols and furans may also occur.

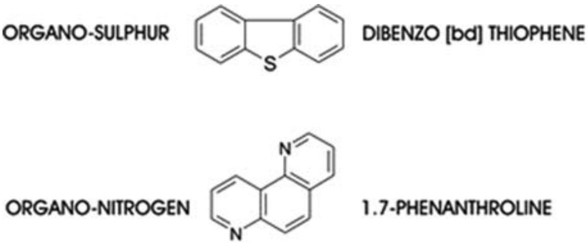

Fig. 1.2 Non-hydrocarbon examples of sulphur- and nitrogen-heterocyclic structures

Finally, there are very high molecular weight resins and asphaltenes which contain a variety of aromatic and heterocyclic structures. Resins are the lower molecular weight, <1000 amu, species, whilst asphaltenes result from linking together many other structures and have exceptionally high molecular weights.

1.2.2 Characteristics of the Hydrocarbons for Lubricant Performance

Only hydrocarbon properties are discussed in this section because most of the non-hydrocarbons are prone to oxidation or degradation and are deleterious to lubricant performance. However, organosulphur molecules are known to act as naturally occurring antioxidants and it is frequently desirable to retain some of these in a refined base oil.

Alkanes, alicyclics and aromatics of the same molecular weight have markedly different physical and chemical characteristics. Physical characteristics affect the viscometrics of the lubricant, and the chemical stability of each class to oxidation and degradation is very important in use.

Alkanes: Of the three main classes, alkanes have relatively low densities and viscosities for their molecular weights and boiling points. They have good viscosity/temperature characteristics, i.e. they show relatively little change in viscosity with change in temperature – see ‘viscosity index’ in Section 1.3.1 – compared to cyclic hydrocarbons. However, there are significant differences between isomers as the degree of alkane chain branching increases, Fig. 1.3.

Linear alkanes, the ‘normal’, or *n*-paraffins in the lubricant boiling range have good viscosity/temperature characteristics but their high melting points cause them to crystallise out of solution as wax. In contrast, highly branched alkanes are not waxy but have less good viscosity/temperature characteristics. There is a compromise region in which acceptable viscosity index, VI, and acceptable low-temperature properties are achieved simultaneously. In general, alkanes also have good viscosity/pressure characteristics, are reasonably resistant to oxidation and have particularly good response to oxidation inhibitors.

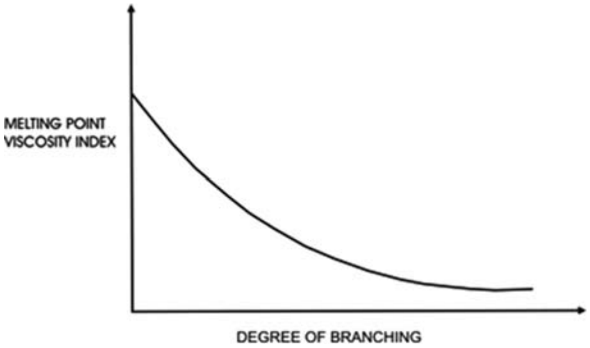

Fig. 1.3 Variation in properties of alkane isomers

Alicyclics have rather higher densities and viscosities for their molecular weights compared to alkanes. An advantage of alicyclics over alkanes is that they tend to have low melting points and so do not contribute to wax. However, one disadvantage is that alicyclics have inferior viscosity/temperature characteristics. Single-ring alicyclics with long alkyl side chains, however, share many properties with branched alkanes and can be highly desirable components for lubricant base oils. Alicyclics tend to have better solvency power for additives than pure alkanes but their stability to oxidative processes is inferior.

Aromatics have densities and viscosities which are yet still higher. Viscosity/temperature characteristics are in general rather poor but melting points are low. Although they have the best solvency power for additives, their stability to oxidation is poor. As for alicyclics, single-ring aromatics with long side chains, alkylbenzenes, may be very desirable base oil components.

1.2.3 Crude Oil Selection for Base Oil Manufacture

Different crude oils contain different proportions of these classes of organic components and also vary in the boiling range distribution of their components. The main factors affecting crude oil selection for the manufacture of base oils are the following:

- content of material of a suitable boiling range for lubricants,
- yield of base oil after manufacturing processes,
- base oil product properties, both physical and chemical.

The manufacturing process at a base oil refinery consists of a series of steps to separate the desirable lube components from the bulk of the crude oil, described in detail in Section 1.4, but briefly, their aims are as follows:

Distillation: removes both the components of too low boiling point and too high boiling point, leaving the lubricant boiling range distillates.
Aromatics removal: leaves an oil that is high in saturated hydrocarbons and improves VI and stability.
De-waxing: removes wax and controls low-temperature properties of the base oil.
Finishing: removes traces of polar components and improves the colour and stability of the base oil.

The yield of base oil after these processes depends on the amount of desirable components in the lubricant boiling range. Lubricant distillates from different crudes can have radically different properties, Table 1.2. Both the Forties and Arabian distillates have relatively high VI and high pour point because they are rich in alkanes and are examples of paraffinic crude oils. Paraffinic crudes are preferred for manufacturing base oils where viscosity/temperature characteristics are important, e.g. for automotive lubricants for operation over a wide temperature range. However, there is a big difference in sulphur content between these two crude oils and this has an effect on base oil composition and its chemical properties, especially natural oxidation stability. Careful control of the manufacturing processes can minimise some of these differences.

Table 1.2 Comparison of lubricant distillates from a range of crude oils

Crude source	North Sea (Forties)	Middle East (Arabian)	Nigeria (Forcados)	Venezuela Field (Tia Juana)
Viscosity at 40°C (cSt)	16	14	18	23
Pour point (°C)	25	19	18	–48
Viscosity index	92	70	42	10
Sulphur content (wt%)	0.3	2.6	0.3	1.6
Aromatics (wt%)	20	18.5	28	21

The Nigerian and Venezuelan distillates are examples of naphthenic products because they are relatively low in alkane content. In particular, the Venezuelan distillate is wax-free and a de-waxing step is not required. Although naphthenic products have inferior viscosity/temperature characteristics, they have other beneficial properties which are particularly useful in industrial applications.

The examples given are all crude oils regularly used to make base oils but many other crudes do not contain sufficient useful lubricant components and cannot be economically used for conventional base oil production. However, in Section 1.5, a modern catalytic process is described which upgrades distillates of less suitable origin and so creates desirable lubricant components.

1.3 Products and Specifications

1.3.1 Introduction

Lubricants are formulated by blending base oils and additives to meet a series of performance specifications, Chapter 17. These specifications relate to the chemical and physical properties of the formulated oil when it is new and also ensure that the oil continues to function and protect the engine or machinery in service. Self-evidently, lubricant performance is determined by the base oils and the additives used in the formulation.

A range of properties can be measured and used to predict performance when selecting an appropriate base oil for use in formulation. Many of these properties are used as quality control checks in the manufacturing process to ensure uniformity of product quality. Although many of these properties are modified or enhanced by the use of additives, knowledge of the base oil characteristics, especially any limitations, is vital for the effective formulation of any lubricant.

The complexity of the chemical composition of the base oils requires that most measurements are of overall, bulk, physical or chemical properties which indicate the average performance of all the molecular types in the base oil. Many tests are empirically based and are used to predict, or correlate with, the real-field performance of the lubricant. Although not rigorously scientific, the importance of such tests should not be underestimated.

A wide range of tests was developed by different companies and different countries in the early days of the oil industry. Many tests are now standardized and controlled on an international basis by organisations such as the following:

USA	American Society for Testing and Materials, ASTM,
UK	Institute of Petroleum, IP (now the Energy Institute),
Germany	Deutches Institut für Normung, DIN,
Europe	Association des Constructeurs Européens d'Automobiles, ACEA,
Japan	Japanese Automotive Standards Organization, JASO,
International	International Organisation for Standards, ISO.

1.3.2 Physical Properties – Viscosity

Viscosity measures the internal friction within a liquid, reflecting the way molecules interact to resist motion. It is a vital lubricant property, influencing the ability of the oil to form a lubricating film or to minimise friction and reduce wear.

Newton defined the absolute viscosity of a liquid as the ratio between the applied shear stress and the resulting shear rate. If two plates of equal area *A* are considered as separated by a liquid film of thickness *D,* as in Fig. 1.4, the shear stress is the force *F* applied to the top plate causing it to move relative to the bottom plate divided by the area of the plate *A*. The shear rate is the velocity *V* of the top plate divided by the separation distance *D*.

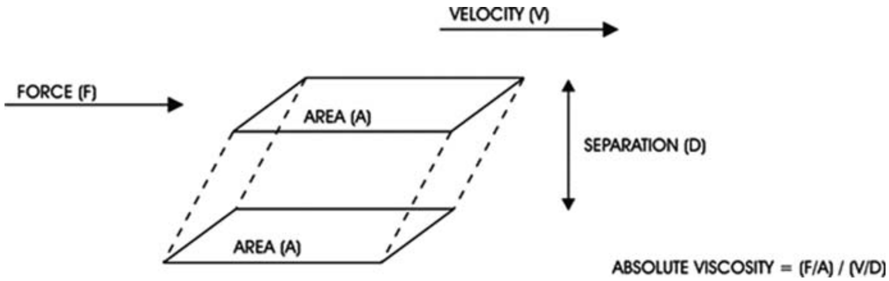

Fig. 1.4 Definition of absolute viscosity

The unit of absolute viscosity is the pascal second (Pa.s), but centipoise (cP) is generally used as the alternative unit, where 1 Pa.s $= 10^3$ cP. Absolute viscosity is usually measured with rotary viscometers where a rotor spins in a container of the fluid to be measured and the resistance to rotation, torque, is measured. Absolute viscosity is an important measurement for the lubricating properties of oils used in gears and bearings. However, it cannot be measured with the same degree of simplicity and precision as kinematic viscosity, defined as the measurement of liquid flow rate through a capillary tube under the constant influence of force of gravity. Kinematic and absolute viscosities are related by Equation (1.1):

$$\text{Kinematic viscosity} = (\text{Absolute viscosity})/(\text{Liquid density}) \qquad (\text{Eqn. 1.1})$$

The unit of kinematic viscosity is m^2/s but for practical reasons it is more common to use the centistoke, cSt, where 1 cSt $= 10^{-6}$ m^2/s. It is routinely measured with ease and great precision in capillary viscometers suspended in constant temperature baths. Standard methods are ASTM D445, IP 71 and several standard temperatures are used. Measuring the kinematic viscosity of a liquid at several temperatures allows its viscosity/temperature relationship to be determined, see immediately below this subsection.

There are other, empirical, scales in use such as SUS (Saybolt Universal Seconds) or the Redwood scales, and conversion scales are available. Base oil grades are sometimes referred to by their SUS viscosities.

Viscosity/temperature relationship – the viscosity index: The most frequently used method for comparing the variation of viscosity with temperature between different oils calculates a dimensionless number, the viscosity index, VI. The kinematic viscosity of the sample oil is measured at two different temperatures, 40 and 100°C, and the viscosity change is compared with an empirical reference scale. The original reference scale was based on two sets of lubricant oils derived from separate crude oils – a Pennsylvania crude, arbitrarily assigned a VI of 100, and a Texas Gulf crude, assigned a VI of 0 [2]. The higher the VI number, the less the effect of temperature on the viscosity of the sample. Full definitions of the calculation methods are given in the ASTM 2270 or IP 226 manuals, summarized in Fig. 1.5. In this figure, *L* is the viscosity at 40°C of an oil of 0 VI which has the same viscosity at

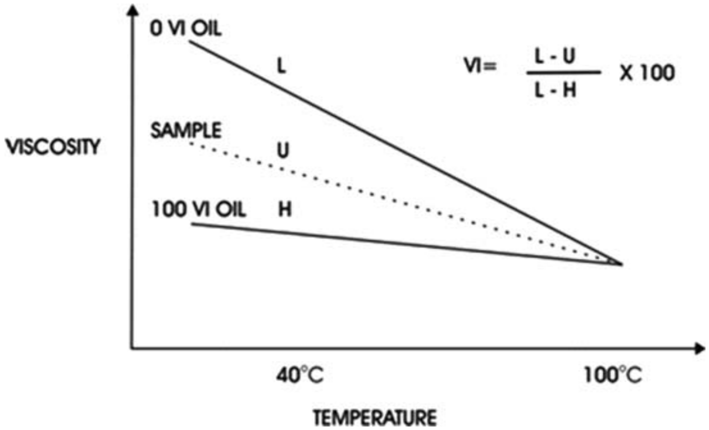

Fig. 1.5 Definition of viscosity index

100°C as the sample under test; *H* is the viscosity at 40°C of an oil of 100 VI which has the same viscosity at 100°C as the sample under test; and *U* is the viscosity at 40°C of the oil sample. *L* and *H* are obtained from standard tables. A modified procedure applies to oils of VI above 100 or to oils of high viscosity.

The VI scale is a useful tool in comparing base oils, but it is vital to recognise its arbitrary base and limitations. Extrapolation outside the measured temperature range of 40–100°C may lead to false conclusions, especially as wax crystals form at low temperatures. VI is also used as a convenient measure of the degree of aromatics removal during the base oil manufacturing process. But comparison of VIs of different oil samples is realistic only if they are derived from the same distillate feed stock. Therefore, great care should be used in applying VI measurements as indicators of base oil quality.

Low-temperature properties: When a sample of oil is cooled, its viscosity increases predictably until wax crystals start to form. The matrix of wax crystals becomes sufficiently dense with further cooling to cause apparent solidification of the oil. But this is not a true phase change in the sense that a pure compound, such as water, freezes to form ice. Although the 'solidified' oil will not pour under the influence of gravity, it can be moved if sufficient force is applied, e.g. by applying torque to a rotor suspended in the oil. Further decrease in temperature causes more wax formation, increasing the complexity of the wax/oil matrix and requiring still more torque to turn the rotor. Many lubricating oils have to be capable of flow at low temperatures and a number of properties should be measured.

Cloud point is the temperature at which the first signs of wax formation can be detected. A sample of oil is warmed sufficiently to be fluid and clear. It is then cooled at a specified rate. The temperature at which haziness is first observed is recorded as the *cloud point*, the ASTM D2500/IP 219 test. The oil sample must be free of water because it interferes with the test.

Pour point is the lowest temperature at which an oil sample will flow by gravity alone. The oil is warmed and then cooled at a specified rate. The test jar is removed from the cooling bath at intervals to see if the sample is still mobile. The procedure is repeated until movement of the oil does not occur, ASTM D97/IP 15. The *pour point* is the last temperature *before* movement ceases, not the temperature at which solidification occurs. This is an important property of diesel fuels as well as lubricant base oils. High-viscosity oils may cease to flow at low temperatures because their viscosity becomes too high rather than because of wax formation. In these cases, the pour point will be higher than the cloud point.

The cold crank simulator test, ASTM D2602/IP 383, measures the apparent viscosity of an oil sample at low temperatures and high shear rates, related to the cold starting characteristics of engine oils, which should be as low as possible. The oil sample fills the space between the rotor and the stator of an electric motor, and when the equipment has been cooled to the test temperature, the motor is started. The increased viscosity of the oil will reduce the speed of rotation of the motor and indicates the apparent viscosity of the oil. The test is comparative for different oil samples rather than an accurate prediction of the absolute performance of an oil in a specific engine.

The Brookfield viscosity test measures the low-temperature viscosity of gear oils and hydraulic fluids under low shear conditions. Brookfield viscosities are measured in centipoise units using a motor-driven spindle immersed in the cooled oil sample, ASTM D2983.

High-temperature properties of a base oil are governed by its distillation or boiling range characteristics. *Volatility* is important because it indicates the tendency of oil loss in service by vapourisation, e.g. in a hot engine. Several methods are used to characterise volatility, including the following:

- the *distillation curve*, measured by vacuum distillation, ASTM D1160, or simulated by gas chromatography, ASTM D2887,
- *thermogravimetric analysis,*
- *Noack volatility*, where the sample is heated for 1 hour at 250°C and the weight loss is measured, DIN 51581.

Flash Point: The *flash point* of an oil is an important safety property because it is the lowest temperature at which auto-ignition of the vapour occurs above the heated oil sample. Different methods are used, ASTM D92, D93, and it is essential to know which equipment has been used when comparing results.

Other physical properties: Various other physical properties may be measured, most of them relating to specialised lubricant applications. A list of the more important measurements includes the following:

Density: important, because oils may be formulated by weight but measured by volume,
Demulsification: the ability of oil and water to separate,
Foam characteristics: the tendency to foam formation and the stability of the foam that results,
Pressure/viscosity characteristics: the change of viscosity with applied pressure,
Thermal conductivity: important for heat transfer fluids,
Electrical properties: resistivity, dielectric constant,
Surface properties: surface tension, air separation.

1.3.3 Chemical Properties – Oxidation

Degradation of lubricants by oxidative mechanisms is potentially a very serious problem. Although the formulated lubricant may have many desirable properties when new, oxidation can lead to a dramatic loss of performance in service by reactions such as:

- corrosion due to the formation of organic acids,
- formation of polymers leading to sludge and resins,
- viscosity changes,
- loss of electrical resistivity.

A variety of different stability tests have been devised to measure resistance to oxidation under different conditions which correlate with different service uses of lubricants. Since oxidation inhibitors are frequently added to base oils, response of the base oil to standard inhibitors is an important measurement and therefore some tests are carried out in the presence of standard doses of antioxidants, see Chapter 4. Other tests include catalysts to cause accelerated ageing of the oil and reduce the duration of testing to manageable periods. The sulphur content of base oils is often regarded as a useful indicator of natural oxidation resistance. This is because many naturally occurring organosulphur compounds in crude oil are moderately effective in destroying organic peroxide intermediates and breaking the oxidation chain mechanism. However, the effectiveness of these natural inhibitors is usually rather inferior to synthesized additives which can be much more specific in their action.

Corrosion: A lubricant base oil must not contain components which corrode metal parts of an engine or a machine. The problems of oxidation products leading to corrosion have been mentioned above and corrosion tests usually involve bringing the base oil sample into contact with a metal surface (copper and silver are often used) under controlled conditions. Discolouration of the metal, changes in surface condition or weight loss may be used to measure the corrosion tendency of the oil.

Other tests have been devised to measure corrosion protection properties of the oil under adverse conditions, e.g. in the presence of water, brine or acids formed as combustion products; however, these tests are more applicable to formulated lubricants rather than base oils.

Carbon residue: A test used to measure the tendency of a base oil to form carbonaceous deposits at elevated temperatures. The Conradson carbon residue test, ASTM D189, determines the residue which remains after pyrolytic removal of volatile compounds in the absence of air.

Seal compatibility: Lubricants come into contact with rubber or plastic seals in machines. The strength and degree of 'swell' of these seals may be affected by interaction with the oil. Various tests measure the effects of base oils on different seals and under different test conditions.

1.3.4 Base Oil Categories: Paraffinics

Paraffinic base oils are produced from crude oils of relatively high alkane content; typical crudes are from the Middle East, North Sea and US mid-continent. This is not an exclusive list, nor does it follow that all North Sea crudes, for example, are suitable for production of paraffinic base oils. The manufacturing process requires aromatics removal (usually by solvent extraction) and de-waxing.

Paraffinic base oils are characterised by good viscosity/temperature characteristics, i.e. high viscosity index, adequate low-temperature properties and good stability. In oil industry terminology, they are frequently called solvent neutrals, SN, where 'solvent' means that the base oil has been solvent refined and 'neutral' means that the oil is of neutral pH. An alternative designation is high viscosity index, HVI, base oil. Most base oils produced in the world are paraffinics and are available over a full range of viscosities, from light spindle oils to viscous bright stock; examples of a range of paraffinic base oils from typical refinery production are given in Table 1.3.

Table 1.3 Paraffinic base oils – typical properties (Arabian crude)

Grade	Spindle	150SN	500SN	Bright stock
Density at 20°C (kg l^{-1})	0.85	0.87	0.89	0.91
Viscosity at 40°C (cSt)	12.7	27.3	95.5	550
Viscosity at 100°C (cSt)	3.1	5.0	10.8	33
Viscosity index	100	103	97	92
Pour point (°C)	–15	–12	–9	–9
Sulphur content (wt%)	0.4	0.9	1.1	1.5

Paraffinic base oils of very high viscosity index are also manufactured by severe hydrotreatment or hydrocracking processes, Section 1.5, in which isoalkanes are created by chemical reaction and their crude oil origin is of reduced importance.

Naphthenics are made from a more limited range of crude oils than paraffinics, and in smaller quantities, at a restricted number of refineries. Important characteristics of naphthenic base oils are their naturally low pour points, because they are wax-free, and excellent solvency powers. Their viscosity/temperature characteristics are inferior to paraffinics, i.e. they have low/medium VI, but they are used in a wide range of applications where this is not a problem. Since naphthenic crudes are free of wax, no de-waxing step is needed but solvent extraction or hydrotreatment is often used now to reduce aromatic content and especially to remove polycyclic aromatics which may present a health hazard in untreated oils. The main producers of naphthenics are in North and South America because most of the world's supply of naphthenic lubricant crudes are found there.

Other base oil categories: Base oil refineries produce a range of other products besides their main output of paraffinic or naphthenic base oils. These products are either by-products or speciality products made by additional process steps or by more severe processing; the main types are the following:

White oils: These are highly refined oils which consist entirely of saturated components, all aromatics being removed by treatment with fuming sulphuric acid or by selective hydrogenation. Their name reflects the facts that they are virtually colourless and the most highly refined. White oils are used in medical products and the food industry.

Electrical oils: Oils used in industrial transformers for electrical insulation and heat transfer must have low viscosity and very good low-temperature properties. They are produced either from naphthenic crudes or by urea/catalytic de-waxing from paraffinic crudes.

Process oils: Lightly refined base oils or highly aromatic by-product extracts from oil manufacture are used in various industrial products, e.g. plasticisers in automotive tyres, in printing inks and in mould release oils.

1.3.5 Safety of Petroleum Base Oils

Several studies have shown that certain categories of poorly or untreated petroleum base oils can cause cancer in humans. The principal molecular types believed to be responsible are the three- to seven-ring polycyclic aromatics. The IP 346 test method selectively extracts these materials from a sample of the base oil and enables their concentration to be estimated, fully described in a CONCAWE report [3]. Base oils are now classified according to this test method for their carcinogenic potential and the labelling of finished lubricant products must now comply with these rules.

1.4 Conventional Base Oil Manufacturing Methods

1.4.1 Historic Methods

Very early lubricants were made by the simple distillation of petroleum to recover the lower boiling gasoline and kerosene fractions to give a residue useable as a lubricant. Lubricant quality could be improved by very simple additional processing to remove some of the less desirable components such as asphalt, wax and aromatics. Lubricants of this era relied on the inherent properties of the base oil because virtually no additives were used.

Vacuum distillation separated lubricant distillates from crude oil, leaving the asphalt behind in the distillation residue. Wax used to be removed by chilling the lube distillate and filtering in plate and frame presses. Aromatics were reduced by treating the oil with sulphuric acid and separating the acid tar phase. Finally, finishing treatments such as adsorption of acid residues and impurities by activated clays gave further improvement in product quality. These processes were mainly batch operations, labour intensive and characterised by their hazardous nature. They were unsuitable for the great expansion in production capacity which the industry was called upon to supply.

New technology developed continuous operations so that plants became much larger and could make more consistent quality products at lower cost. These new process methods were based on the use of solvents: continuous selective solvent extraction for aromatic removal was the process which replaced acid treatment and continuous solvent de-waxing replaced the very labour-intensive cold-pressing technique. Technology has developed further in the last 40 years. Catalytic hydrogenation processes have become the normal method for finishing base oils and a more severe form is used as an alternative to solvent extraction to control aromatics content.

With the exception of these newer hydrotreatment processes, all other processes used in modern base oil plants are physical separation techniques, i.e. all the essential constituents of the finished base oil were present in the original crude oil and processing methods are used to concentrate the desirable components by removing the less desirable components as by-products.

1.4.2 Base Oil Manufacture in a Modern Refinery

Most base oil plants are integrated with mainstream oil refineries which produce a range of transportation and heating fuel products. Overall production capacity for lubricant base oils is a very small part of total refinery throughputs, amounting to less than 1.3% in America [4].

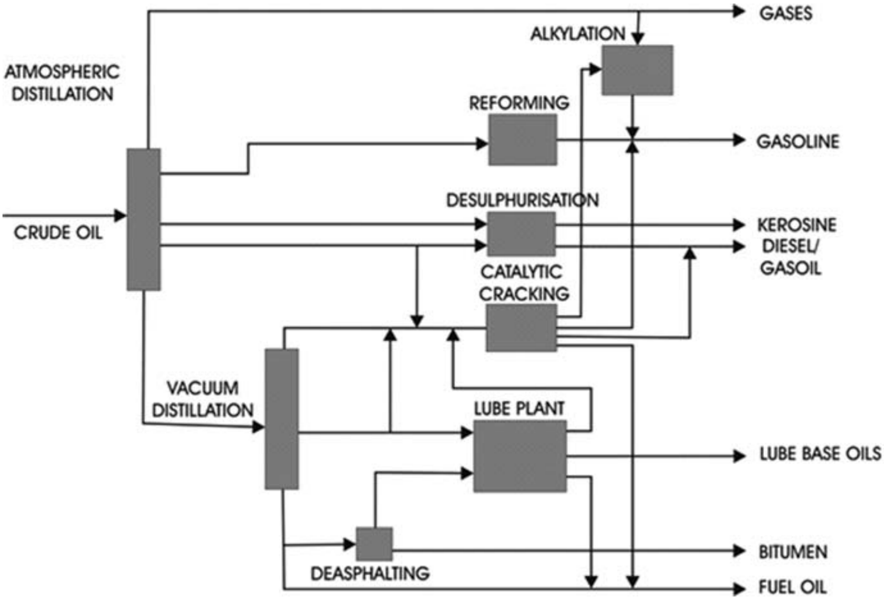

Fig. 1.6 Simplified refinery flow scheme

Figure 1.6 indicates where a lubricant base oil plant fits into the process flow scheme of a ‘typical refinery’ – if ever there is such a thing. Although the scheme is simplified, the inter-relationship between the base oil plant and other process units and product streams is evident. In a sense, the base oil plant and the fuel-upgrading plant, such as the catalytic cracker, compete for feedstock from vacuum distillation. These interactions are very important to the logistics and production economics of producing base oils.

Base oil manufacture produces large quantities of by-products, the unwanted components of the crude oil. Figure 1.7 is a typical base oil production flow scheme where the numbers indicate the relative amounts of intermediate and final product throughout the manufacturing process. The basis for the scheme given is processing the residue from the atmospheric distillation of a good-quality Middle East crude. Starting with 100 parts of residue, which in itself represents only about 50% of the original crude oil, even when the maximum possible amount of each base oil is produced, only 24 parts of base oil result. In practice, the demand for grades of different base oils is unlikely to match the possible output of each grade and surplus distillate and residue is returned to the main fuel production part of the refinery. It is quite normal for the actual output of base oil to be less than 10% of the crude oil purchased for making base oil.

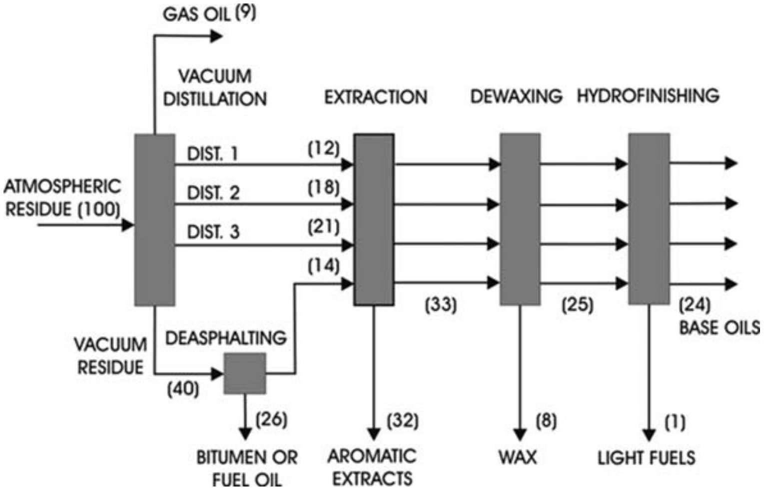

Fig. 1.7 A typical base oil production unit flow scheme

Since the choice of crude oil is restricted when making base oils, the production of relatively small volumes of base oil makes a large imposition on the crude purchasing requirements of a refinery. If suitable crudes are only available at a premium price, then there is an economic penalty for the refinery. Consequently, in recent years refining companies have given considerable effort to expand the portfolio of crude oil which they can use to make satisfactory base oils, giving more flexibility in crude oil purchasing.

1.4.3 Base Oil Production Economics

Each oil refinery is different, with different process units and different relative production capacities arranged in different schemes to make different product ranges. Thus, any view of production economics must, of necessity, be generalised. Production costs can be divided into several categories:

- net feedstock or hydrocarbon cost of making base oil,
- variable operating costs (e.g. energy, chemicals),
- fixed operating costs (e.g. wages, maintenance, overheads),
- costs of capital (e.g. depreciation, interest).

Production costs per tonne of base oil are calculated by dividing the total annual costs by the total annual production of base oils. Net feedstock cost can be calculated in several ways, but it will not necessarily be identical to the cost of crude oil. As the base oil plant in a sense competes with fuel production units for feedstock, the basic feedstock cost to the lubricant base oil complex should be determined by the alternative value of that feedstock if it were used to make mainstream fuels products. The by-products of base oil manufacture also have values for blending into fuel streams or in some cases for direct sale as speciality products, such as waxes and bitumen. Credit must be given for these products so that the net value of the hydrocarbon content of the base oil can be calculated. Refineries use sophisticated linear programming computer models to optimise refinery operations based on different crude oil input, process yields, market prices, production targets, etc.

Variable and fixed operating costs are usually well defined but when these costs are divided by the relatively small output of base oil, they are seen to be significant. If the base oil plant operates below maximum capacity, then the fixed costs have to be shared over an even smaller volume and overall production costs rise in proportion. Energy costs are high because of the number of process steps needed and the energy-intensive nature of equipment such as refrigeration plant and solvent recovery systems. Energy use will vary between refineries, but consumptions as high as 0.4 tonnes fuel oil equivalent per tonne of base oil product are not uncommon.

The costs of capital tend to relate to the age of the base oil plant. A brand new plant has to be financed and since base oil production plant is very expensive to build, depreciation and interest charges will be considerable. Much present day base oil plant is at least 25 years old and so, by now, is almost depreciated. Therefore, for many base oil refineries the cost of making base oil is limited to the hydrocarbon value and operating costs, which make it generally a profitable activity.

1.4.4 Distillation

The primary process for separating the useful fractions for making lubricant base oils from crude oil is distillation. Crude oil is distilled at atmospheric pressure into components of gases, naphtha, kerosene and gas oil, essentially those boiling below 350°C, and a residue containing lubricant base oil boiling range components.

Thermal decomposition increasingly occurs at higher temperatures and further separation by distillation of the atmospheric residue into lubricant base oil is carried out in a vacuum unit, Fig. 1.8. Atmospheric residue feedstock is injected with steam and pre-heated in a furnace before entering the lower part of the vacuum column. Inside the column, a variety of different mechanical arrangements are used to assist separation of different boiling range fractions:

- trays, placed at intervals, with holes, bubble caps or valves to allow rising vapour and falling liquid to contact each other and come to equilibrium,
- packing with randomly arranged rings or other particles, giving a high surface area for liquid/vapour contact,
- packing with geometrically structured mesh, giving excellent contact and distribution of liquid and vapour.

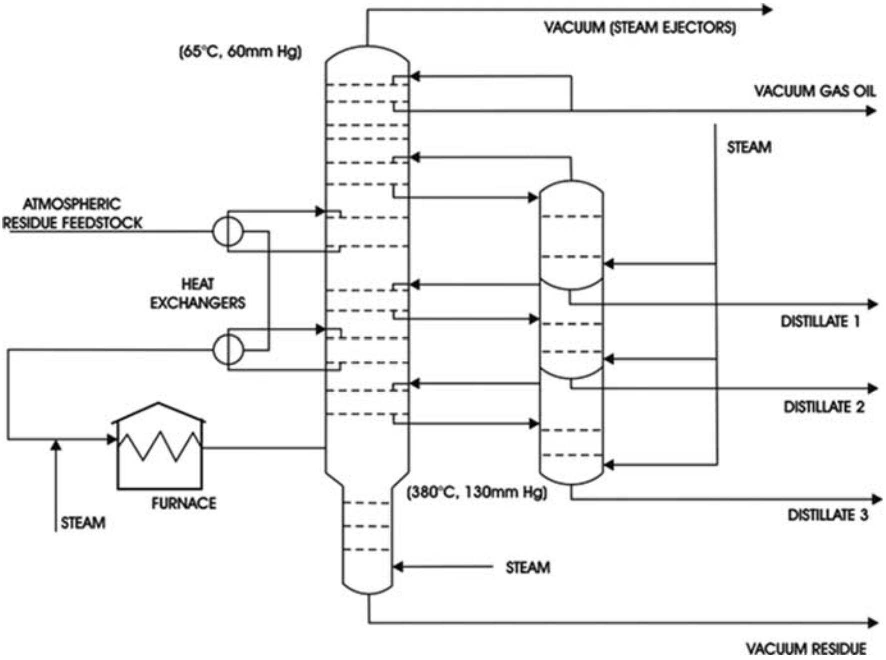

Fig. 1.8 Lubricant base oil vacuum distillation unit

Vacuum is applied at the top of the column, normally by steam ejectors which use condensing steam to create a vacuum, sometimes by vacuum pumps. Pressure in the flash zone is likely to be in range of 100–140 mm Hg. Injection of superheated steam helps to reduce the partial pressure of hydrocarbons in the flash zone, aiding separation of the heavy distillate from the residue and restricting overheating. From the flash zone the mixture of vapourised hydrocarbons and steam passes upwards and the condensed liquid descends. A temperature gradient is created through the column, from ~140°C near the top to ~360°C at the base by taking several side streams from selected trays at different levels in the column and cooling the streams before re-injection at a higher level. The required lubricant distillates are also withdrawn as sidestreams and are steam stripped to give the best possible separation between each fraction. A residue, typically boiling above 550°C at atmospheric pressure, is drawn from the column base. Distillation provides a limited number of fractions, usually three lubricant distillates, each of which has a viscosity and boiling range defined within a narrow range, and a residue. The quality and consistency of fractionation has considerable impact on all the subsequent process steps. Careful design and operation of the vacuum column should achieve the following desirable results:

- minimum overlap in boiling range between fractions, noting however that some overlap is inevitable,
- avoidance of entrained high molecular weight asphaltic components in the heaviest distillate fraction,
- ability to take a very heavy distillate fraction, rather than losing this material in the distillation residue,
- flexibility to run different crudes and still achieve design specifications for the properties of each lube fraction,
- minimum energy usage.

Use of structured packing in past years together with good design of the flash zone region of the column has helped to achieve these aims on modern base oil plants. Re-vamping and modernisation of older columns has also given substantial benefits. The lubricant distillates and residue streams are run to heated intermediate tankage from where they are drawn to feed downstream process units.

1.4.5 De-asphalting

The residue from vacuum distillation is a black, very viscous material containing large amounts of asphaltic and resinous components. When these are removed, a useful high-viscosity base oil fraction, known as bright stock, is left. Low molecular weight hydrocarbons as solvents are effective at dissolving the more desirable compounds whilst leaving the asphaltic material as a separate phase. Liquid propane is by far the most frequently used solvent for de-asphalting residues to make lubricant bright stock, whereas liquid butane or pentane produces lower grade de-asphalted oils more suitable for feeding to fuel-upgrading units.

The liquid propane is kept close to its critical point and, under these conditions, raising the temperature increases selectivity. A temperature gradient is set up in the extraction tower to facilitate separation. Solvent-to-oil ratios are kept high because this enhances rejection of asphalt from the propane/oil phase. Counter-current extraction takes place in a tall extraction tower, of the type in Fig. 1.9. Vacuum distillation residue enters near the top of the tower, while propane enters near the base. The de-asphalted oil/propane phase, being lower in density, is taken from the top of the tower and the heavy asphalt phase leaves at the bottom. Steam heating coils provide the temperature gradient within the tower. Typical operating conditions are the following:

• propane/vacuum residue volume ratio	between 5–10:1
• pressure	25–35 bar
• top temperature	60–80°C
• base temperature	30–40°C

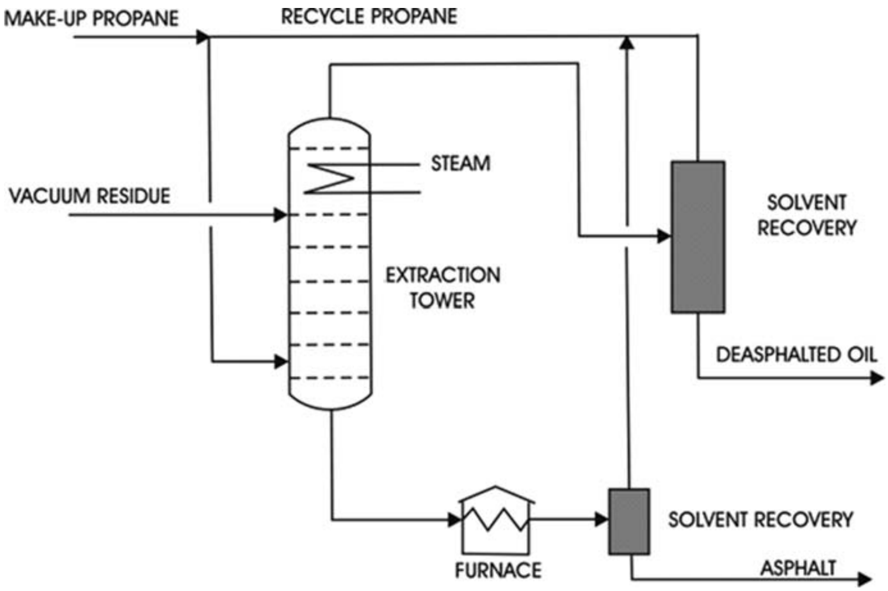

Fig. 1.9 Propane de-asphalting unit

Good contact of feedstock and propane is essential and a variety of tower internal arrangements are used to achieve this target:

- tower packed with random particles, e.g. ceramic,
- baffles or trays,
- mechanical rotating disc contactors.

The bulk of the de-asphalting plant comprises equipment for solvent recovery for the de-asphalted oil and asphalt phases and also cooling and compression for recycling of the propane solvent. The de-asphalted oil product is a viscous, waxy material and requires solvent extraction and de-waxing before it can be used as a base oil. The asphalt is a valuable feedstock for making bitumen grades or for blending into fuel oil.

1.4.6 Solvent Extraction

Solvent extraction replaced acid treatment as the method for improving oxidative stability and viscosity/temperature characteristics of base oils. The solvent selectively dissolves the undesired aromatic components, the extract, leaving the desirable saturated components, especially alkanes, as a separate phase, the raffinate. Choice of solvent is determined by a number of factors, which are as follows:

- selectivity, i.e. to give good yields of high-quality raffinate,
- solvent absorption power, to minimise the solvent/oil ratio,
- ease of separation of extract and raffinate phases,
- ease of solvent recovery – its boiling point must be below that of the raffinate extract,
- desirable solvent properties such as stability, safety, low toxicity, ease of handling and cost.

New plant units and conversions increasingly use *N*-methylpyrrolidone because it has the lowest toxicity and can be used at lower solvent/oil ratios, which save energy. Solvents used commercially include:

– sulphur dioxide, historically important but rare nowadays,
– phenol, now declining in use,
– furfural, the most widely used,
– *N*-methylpyrrolidone, increasing in importance.

Each distillate or bright stock stream is processed separately because different process conditions are needed to obtain optimum results for each base oil grade. The main factors in operation of such a plant are the following:

Solvent/oil ratio: Increasing the solvent/oil ratio allows deeper extraction of the oil, removing more aromatics and, of course, decreasing the raffinate yield. Over-extraction should be avoided because good lubricant components may be lost.

Extraction temperature: Solvent power increases with temperature, but selectivity decreases until feed and solvent become miscible. Clearly, the extreme of complete miscibility must not be allowed. The use of temperature gradients in extraction towers aids selectivity.

Solvent/oil contact: The solvent and oil streams must be brought into contact, mixed efficiently and then separated into solvent and raffinate phases. The principal methods used are the following:

– multi-stage mixing vessels, arranged in series so that flows of solvent and oil run counter-currently,
– extraction towers packed with ceramic rings or with sieve trays. Flows of solvent and oil are counter-current as described in Section 1.4.5 on the de-asphalting plant. A temperature gradient is maintained within the tower,
– extraction towers using a vertically mounted ‘rotating disc contact’. The spinning discs alternate with wall-mounted baffles and create a high shear mixing regime around the discs and allow excellent mixing. Rotor speed can be used as a control mechanism,
– multi-stage centrifugal extractors both mix the incoming solvent and oil streams and separate the raffinate and extract products. They have advantages of small size and small hold-up volume.

Whichever contacting method is used, the end result is two product streams. The raffinate stream is mainly extracted oil containing a limited amount of solvent, while the extract stream is a mixture of solvent and aromatic components. The streams are handled separately during solvent recovery and the recovered solvent streams are recombined and recycled within the plant. A large proportion of an extraction plant is allocated to solvent recovery and is an energy-intensive part of the process.

As mentioned above, feedstocks are run individually (so-called ‘blocked operation’) so that the required properties for each base oil grade can be met economically. If a very wide boiling range feedstock were to be solvent extracted, then at one extreme of the boiling range, over-extraction occurs, while at the other end, under-extraction results. The result is a poor yield of indifferent quality product. Normal refinery operating procedure is to process each base oil grade in turn, drawn from intermediate product tanks, minimizing changes between dissimilar grades, i.e. processing up and down the viscosity range. This avoids major changes in operating conditions and minimises wastage of mixed fractions during changeover.

1.4.7 Solvent De-waxing

The material which crystallises out of solution from lubricant distillates or raffinates is known as wax. Wax content is a function of temperature. As the temperature is reduced, more wax appears. Sufficient wax must be removed from each base oil fraction to give the required low-temperature properties for each base oil grade. Naphthenic feedstocks, of course, are relatively free of wax and do not normally require de-waxing.

The molecular types within the wax fraction change as the boiling range of the feedstock increases. Linear alkanes crystallise easily in the form of large crystals and these are the predominant constituent of wax in the lighter distillates. Isoalkane waxes form smaller crystals and these predominate in the heavier fractions. In addition, as the temperature of de-waxing decreases, the molecular composition of the wax which crystallises out of solution also changes; the highest melting point components crystallise first. Different grades of wax can be separated from different viscosity feedstocks at different temperatures.

The original de-waxing method involved cooling the waxy oil and filtering with large plate and frame presses. Pressures up to 20 bar were applied to the wax cake to force the oil out. However, the process had severe drawbacks, being very labour intensive and oils of high viscosity could not be filtered at low temperatures. Filtration efficiency was greatly improved by diluting the oil with solvents such as naphtha, but selectivity for wax removal was reduced. Improved solvent systems have been developed to give better de-waxing performance. Important factors in the choice of solvent are the following:

- good solubility of oil in the solvent and low solubility of wax in the solvent,
- small temperature differences between the de-waxing temperature and the pour point of the de-waxed oil,

- minimum solvent/oil ratios,
- formation of large wax crystals, which are easily filtered,
- ease of solvent recovery, i.e. low boiling point,
- desirable properties such as stability, safety, low toxicity, ease of handling and cost.

Solvents in commercial use include propane, methyl isobutyl ketone and also mixed solvents such as methyl ethyl ketone/toluene or methylene dichloride/dichloroethane. Using paired solvents helps to control oil solubility and wax crystallisation properties better than using a single solvent.

A simplified flow scheme for a modern solvent de-waxing plant is shown in Fig. 1.10. Solvent and oil are mixed together, then progressively chilled to the required temperature for filtration, which will be several degrees lower than the desired pour point. The rate of chilling influences the size and form of the wax crystals and the subsequent ease of filtration. Chilling takes place in special heat exchangers with mechanically driven scrapers to keep the pipe walls clear of solidifying wax, aid heat transfer and ensure that the oil/wax/solvent slurry remains mobile. Filtration is carried out on large rotary drum filters with suction applied to the inside of the horizontally mounted drum which slowly rotates with the lower part of the drum immersed in the chilled slurry. As oil passes through the filter cloth, a layer of wax (about 0.5 cm thick) builds up on the cloth and is later removed by a scraper blade or blown off by inert gas as the drum rotates.

The de-waxed oil/solvent and the crude wax are handled as separate streams for solvent recovery. The wax contains an appreciable amount of oil because filtration

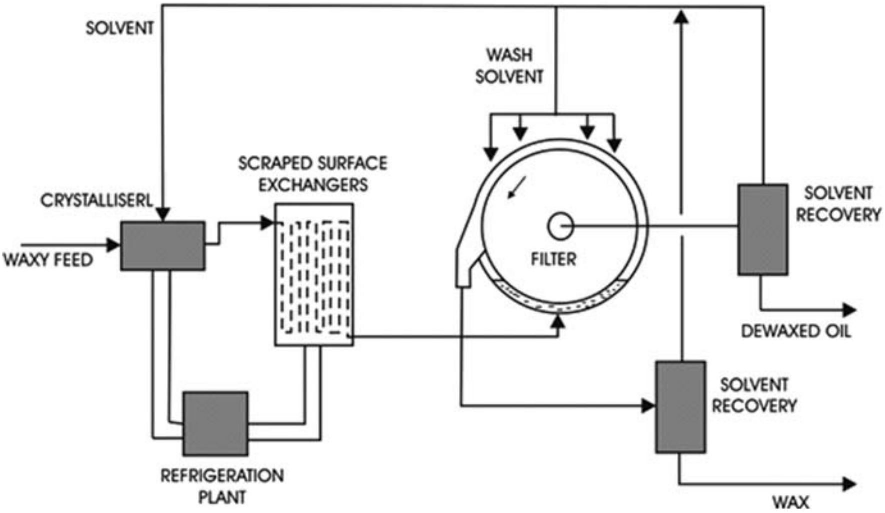

Fig. 1.10 Solvent de-waxing plant

pressures are very low and this oil can be removed by a second filtration stage which also yields high-quality treatment wax products.

If very low pour points are necessary, the costs of extensive de-waxing become very high and the yields correspondingly low. A variant of solvent de-waxing, urea de-waxing, is effective for making low-pour-point base oils. It uses the effect that crystallising urea forms crystals containing linear channels which trap linear alkanes, i.e. wax. The urea–wax adduct is removed by filtration to leave a very low-pour-point oil. Urea and solvent are recovered and recycled.

1.4.8 Finishing

Despite the intensive series of process steps carried out so far, trace impurities may still be present in the base oil and a finishing step is needed to correct problems such as:

- poor colour,
- poor oxidation or thermal stability,
- poor demulsification properties,
- poor electrical insulating properties.

These undesirable components tend to be nitrogen-, oxygen- or, to a lesser extent, sulphur-containing molecules. In the past, selective adsorbents such as clay or bauxite were used to remove impurities but these processes were messy and gave waste disposal problems.

Hydrofinishing has almost completely taken over now and differs from all the process steps described previously because it is not a physical separation procedure. It depends on the selective, catalysed hydrogenation of the impurities to form harmless products under relatively mild conditions. Yields of finished base oil are high (at least 95%) and costs are quite low. Hydrofinishing should be effective for removing organonitrogen molecules because they are largely responsible for poor colour and stability of base oils, while organosulphur molecules should be retained because they tend to impart natural oxidation stability to the base oil.

A simplified flow diagram of a hydrofinishing plant is shown in Fig. 1.11. Oil and hydrogen are pre-heated and the oil allowed to trickle downwards through a reactor filled with catalyst particles where hydrogenation reactions take place. The oil product is separated from the gaseous phase and then stripped to remove traces of dissolved gases or water. Typical reactor operating conditions for hydrofinishing are the following:

- catalyst temperature, 250–350°C,
- operating pressure, 20–60 bar,
- catalyst type, Ni, Mo supported on high-surface-area alumina particles.

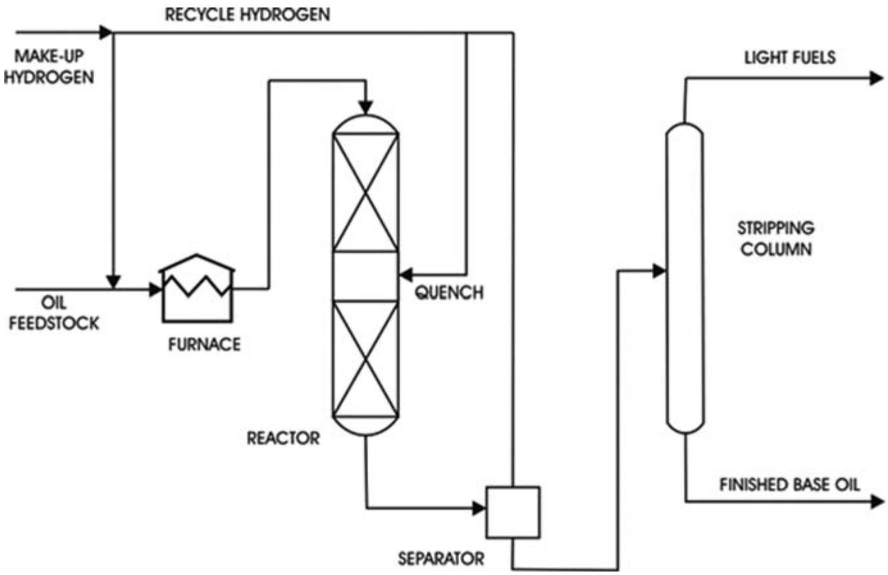

Fig. 1.11 Flow diagram of hydrofinishing unit

1.5 Modern Catalytic Processes

In recent years the solvent-based separation processes have faced competition from new processes based on catalytic hydrogenation as an alternative means of removing unwanted components from the base oil. Hydrogenation offers economic advantages over solvent processes and gives products that are clearly differentiated from conventional solvent-refined base oils. Some catalytic hydrogenation processes go further and create new and highly desirable components. The resulting base oils have characteristics which are superior to anything that could be made by conventional solvent-refining technology relying on physical separation processes. The reactions occurring in catalytic hydrogenation processes are the following:

- hydrogenation of aromatics and other unsaturated molecules,
- ring opening, especially of multi-ring molecules,
- cracking to lower molecular weight products,
- isomerisation of alkanes and alkyl side chains,
- desulphurisation,
- denitrogenation,
- reorganisation of reactive intermediates, e.g. to form traces of stable polycyclic aromatics.

The extent to which each of these reaction types occurs is determined by the type of catalyst used, the process conditions and the feedstock composition. It should always be remembered that the more extensive/severe the hydrotreatment, the higher the energy consumption and the lower the overall yield.

1.5.1 Severe Hydrotreatment

A mild version of this process has already been described in Section 1.4.8 as the hydrofinishing step at the end of a conventional base oil production scheme. Under much more severe operating conditions, hydrogenation of aromatics and ring opening reactions become important and the result is to substantially reduce the aromatic content of the lube distillate. Reactions, however, are not limited to hydrogenation and ring opening. Chain-breaking or hydrocracking reactions which lead to molecular weight reduction are also very important. The distillate feedstock is converted to a range of lower boiling point products such as naphtha, kerosene and gas oil, in addition to material which remains within the lubricant component boiling range.

The lubricant range products have high VI and are analogous to the products made by solvent extraction of distillates, but with important differences. Denitrogenation and desulphurisation reactions lead to products of extremely low sulphur and nitrogen content. Severe hydrotreatment chemically changes the molecular composition, destroying some kinds of molecules and creating other kinds which have good VI properties. Thus the chemical properties and some physical properties of severely hydrotreated base oils are not quite the same as solvent-refined base oils.

Severe hydrotreatment actually decreases the range of molecular types within the base oil, compared to solvent-extracted base oils. Hydrotreated base oils produced from different crude oils have more consistent properties than solvent-extracted oils made from different crude oils. Since the hydrotreating reactions create high-VI molecules, it is possible to produce base oils from crude oils with an inherently low content of higher VI components and would normally be unsuitable for conventional solvent refining [5].

Production of base oils by this route is sometimes described as lubricant oil hydrocracking because it is really a variant of the common refinery process of hydrocracking to make light fuel products from vacuum distillate feedstocks. It is not a complete process for making base oils. Distillation, de-waxing and usually also hydrofinishing steps are needed, just as in a conventional lube plant.

The catalysts used for severe hydrotreatment are specialised types of hydrocracking catalyst. Normally they use sulphides of metals from Groups VI to VIII of the Periodic Table, Mo, W, Ni, Co, supported on a high surface area, high acidity base such as alumina or silica–alumina. Although aluminosilicate zeolites are often used as supports for hydrocracking catalysts, they are preferred for processes which make light fuel products rather than lubricant products. The catalysts are manufactured as mechanically strong particles by extrusion, tabletting or spheridisation so that they can be packed by the tonne to make a porous catalyst bed inside the reactor vessel.

A severe hydrotreating plant will have a flow scheme similar to the hydrofinishing unit shown in Fig. 1.11. Hydrocracking is a highly exothermic reaction, so cold hydrogen must be injected at several points in the catalyst bed to moderate the temperature rise. Operating conditions are severe, with pressures of 100–180 bar and reaction temperatures of 350–420°C.

Because the hydrocracking process changes the boiling range of the oil, the feedstock need not be a narrow range distillate, as is desirable for conventional solvent processing. It must, however, contain a substantial proportion of high boiling components or there will be a very poor yield of lubricant boiling range product.

1.5.2 Special Base Oils from Hydrocracking

The severe hydrotreatment process described previously is an alternative route to the manufacture of high-VI base oils from conventional solvent extraction technology. If the hydrotreatment is made still more severe, then hydrocracking becomes the dominant mechanism and the yield of material remaining within the useful lubricant boiling range can fall drastically from 40–70 to 5–15%. Under these conditions, aromatics destruction is largely complete and the potential base oil product is highly paraffinic. Such a base oil has advantages over ordinary hydrotreated or extracted base oils for its viscosity index is higher and volatility is lower than that for a conventionally produced oil of the same viscosity. These are important benefits for formulating automotive engine lubricants. Although the natural oxidation stability of these special very high-VI base oils is unremarkable, the response to additives such as inhibitors and viscosity index improvers is particularly good. In many respects, these base oils approach the desirable characteristics of synthetic polyalphaolefin (PAO) base oils, see Chapter 2, but are considerably less expensive to manufacture.

An existing lube hydrocracker can be operated at higher severity to make this special product, but the sharp reduction in yield may not be attractive for the base oil plant economics. However, an alternative source of hydrocracked base oil is available from some of the many existing fuel crackers. These hydrocrackers are important refinery conversion units and are used to make a range of fuel products from vacuum distillate feedstocks. Some plants do not fully convert the feed in one pass to low-boiling products and the limited amount of residue which remains, 5–10%, can be recycled within the plant, used as a fuel oil blending component or upgraded to make the special base oils.

Further processing of the hydrocracker residue is needed and Fig. 1.12 indicates the extra steps. Extraction and hydrotreatment are desirable to remove traces of polycyclic aromatics and improve product quality. De-waxing is essential because the hydrocracker residue is invariably waxy and distillation is needed to adjust boiling range and viscosity of the base oil. The economics of making special base oils from fuel hydrocracker residue are determined both by the hydrocracker operation and the additional processing at a conventional base oil plant, which is often at a separate site.

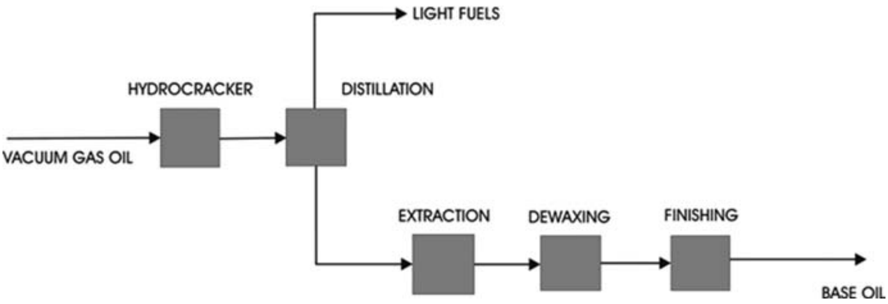

Fig. 1.12 Scheme for hydrocracked oil

1.5.3 Special Base Oils by Wax Isomerisation

Another variant of the severe hydrotreatment process is the substitution of wax for lubricant distillate as feedstock. The wax recovered from conventional solvent dewaxing units is essentially a pure alkane feedstock containing a high proportion of linear alkanes. With this type of feedstock and under appropriate operating conditions, the isomerisation reaction can be made to predominate over cracking reactions. Unconverted wax can be removed by conventional methods to yield a base oil that is exclusively composed of isoalkanes and that resembles synthetic polyalphaolefin base fluids more closely than the hydrocracked base oils described in Section 1.5.2. A comparison of some of these base fluid properties is shown in Table 1.4.

Table 1.4 Base fluid comparisons

Base fluid	Solvent refined	Wax isomerised	Hydrocracked	Polyalphaolefin
Viscosity at 100°C	5.2	5.6	5.0	5.8
Viscosity index	98	125	146	137
Pour point (°C)	–15	–15	–18	–60

Synthetic polyalphaolefins are composed of a very limited number of branched alkane isomers, all having approximately the same molecular weight and also completely wax-free. The wax isomerisation product has a wider spread of isomers and covers a broad band of different molecular weights. It also contains some wax and these products cannot match the low-temperature properties of the polyalphaolefins.

A process flow scheme for making wax-isomerised base oils is shown in Fig. 1.13. The wax feedstock reacts over a catalyst in a hydrogen atmosphere but despite control of conditions to favour isomerisation, a significant amount of cracking to lighter products is inevitable. Products are separated by distillation and the lubricant boiling range material is conventionally de-waxed. The unconverted wax can be recycled to increase the overall base oil yield. The isomerisation reactor may be part of a purpose-built plant or it may be able to use an existing lube hydrocracker [6]. Such a dual purpose plant will be operated for some periods as a severe hydrotreater to make normal VI base oils and for other periods as an isomerisation unit to make the special base oils.

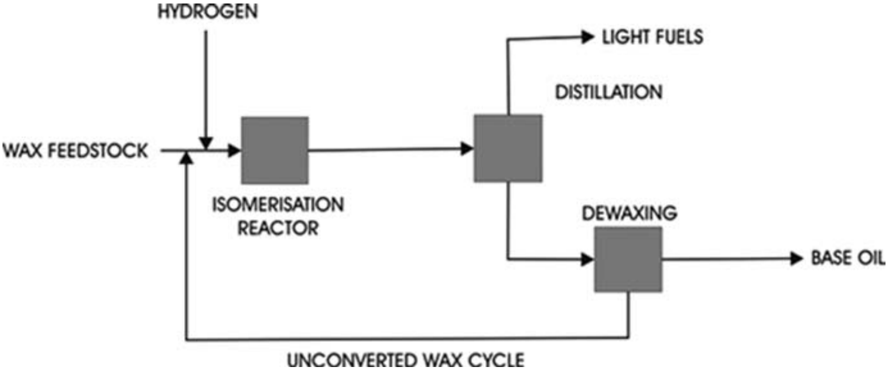

Fig. 1.13 Scheme for wax-isomerised base oils

1.5.4 Catalytic De-waxing

In catalytic de-waxing, special shape-selective catalysts are used to selectively hydrocrack only the straight-chain alkanes to low boiling point by-products. Since it is the linear alkanes that comprise the bulk of the waxy components in the lube boiling range, the oil is effectively de-waxed. There are differences in the composition and properties of base oil de-waxed by catalytic solvent processes because of different selectivities.

De-waxing catalysts are based on molecular sieves such as zeolites or silicalite, which have highly porous structures based on a regular arrangement of channels. The channel openings have diameters of 50–70 nm which will admit only linear or very lightly branched alkanes. Non-waxy branched alkanes and cyclic structures cannot enter the pore structure and so are not converted, although long alkyl side chains on aromatic or alicyclic nuclei can be stripped off. Side chain removal may lead to the loss of some beneficial molecules which have good lubricant performance and are still non-waxy. In contrast, solvent de-waxing separates only those molecules which have crystallised under the de-waxing conditions. Since there is always some good oil trapped in the filter cake of wax, there is also a loss of useful molecules in solvent de-waxing, but these molecules are not the same as those lost by the catalytic route.

The cracking of alkanes initially produces unsaturated, low molecular weight by-products which can polymerise and, through coke formation, cause a rapid loss of catalyst activity. This problem can be minimised by using a zeolite with low coke-forming tendencies, e.g. ZSM-S, or by incorporation of a hydrogenation function, e.g. Pt, Pd, into the de-waxing catalyst. In the latter case, the oil is simultaneously de-waxed and hydrofinished, whereas in the former case, a separate hydrotreatment step is necessary to give a stable product, therefore a separate reactor and catalyst system must be provided. Components such as platinum require greater protection from catalyst poisons, but the molecular sieve action of the catalyst automatically tends to protect the active catalytic sites from many potential poisons which are too large to enter the pores.

Catalytic de-waxing is highly selective for linear alkanes and, since these molecules have the highest VI characteristics, it is usual for catalytically de-waxed base oil to have lower VIs than solvent de-waxed oils of the same pour point. However, it is interesting to observe that the directly measured low-temperature properties such as cold crank simulator and Brookfield viscosities are actually superior for the catalytic products. This is explained by the fact that the molecules of highest melting point have a tendency to form wax gels and are removed more selectively by the catalytic process. The catalytic process is especially effective for the production of very low-pour-point oils from paraffinic crudes that can be replacements for scarce naphthenic oils or for special winter grade lubricants.

A catalytic de-waxing plant resembles other hydrotreating plants and operating condition need not be particularly severe. Operating costs can be significantly less than solvent de-waxing, especially for low-pour-point oils where refrigeration costs become prohibitive [7, 8].

1.5.5 Iso-de-waxing

This process is a development of those described in the previous two sections, namely wax isomerisation and de-waxing, as the ‘Chevron Iso-de-waxing process’ [9]. Whereas the conventional catalytic de-waxing processes selectively hydrocrack wax to low molecular weight by-products, in iso-de-waxing the wax molecules are isomerised and remain within the boiling range of the base oil. The result is to improve both de-waxed oil yields and viscosity index by the retention of very high-VI isoalkane molecules. By careful selection of feedstock and operating conditions, this process can be used to manufacture very high-VI base oils of the type described in Sections 1.5.2 and 1.5.3.

1.6 Categorisation of Base Oils

For many years the quality of lubricant base oils has been categorised by the American Petroleum Institute, API, into ‘Groups’ and used in lubricant specifications worldwide [10]. The latest base oil categories are described in API 1509 (API 2007); only the first three Groups, the mineral oil-derived, non-synthetic, base oils, are described in this chapter. The full categorization, to include up to Group V, is described and discussed in the next chapter. Groups I–III base oils are defined as follows:

- *Group I* base stocks contain less than 90% saturates and/or greater than 0.03% sulphur and have a viscosity index greater than or equal to 80 and less than 120,
- *Group II* base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulphur and have a viscosity index greater than or equal to 80 and less than 120,
- *Group III* base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulphur and have a viscosity index greater than or equal to 120.

These categories are summarized in Table 1.5.

Table 1.5 API categorisation of Group I–III base oils [10]

Categorisation	Saturates (%)	Sulphur (%)	Viscosity index
Group I	< 90	≥ 0.03	$\geq 80, < 120$
Group II	≥ 90	0.03	$\geq 80, < 120$
Group III	≥ 90	0.03	≥ 120

In general, base oils produced by older technologies such as solvent refining and de-waxing are in Group I, whereas hydroprocessing technologies are needed to produce Group II and Group III base stocks. With the continued development of refining processes and the market pressures for cost-effective base oils to meet the latest engine lubricant specifications, these categories have become blurred and there are now unofficial subdivisions of these API categories. As each categorization of Groups I–III defines a band or range of properties, the '+' categories in each Group are base oils with sulphur, saturate concentrations and VIs towards the upper, favourable boundary of their quality bands. The main subdivisions are Group II+ and III+, with 'Group II+' having VIs of 110–120 with improved low-temperature and volatility characteristics. 'Group III+' have VIs approaching, if not exceeding, those of the synthetic PAOs, i.e. above 140. For comparison, 'gas-to-liquid', GTL, base oils, see Chapter 2, are Group III+ with typical viscosities of 4–6 cSt at 100°C and are also very pure with zero sulphur, nitrogen, aromatics and olefins.

The benefit of hydroprocessing of mineral base oils to produce Group II (and II+) and Group III (and III+) is to give consistently lower sulphur and higher saturate concentrations and also higher viscosity indices. The increased consistency of lower sulphur and higher saturate concentration together with higher VIs for these base oil Groups is advantageous for formulating lubricant products [11].

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Chapter 2
Synthetic Base Fluids

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Abstract The chemical nature and technology of the main synthetic lubricant base fluids is described, covering polyalphaolefins, alkylated aromatics, gas-to-liquid (GTL) base fluids, polybutenes, aliphatic diesters, polyolesters, polyalkylene glycols or PAGs and phosphate esters. Other synthetic lubricant base oils such as the silicones, borate esters, perfluoroethers and polyphenylene ethers are considered to have restricted applications due to either high cost or performance limitations and are not considered here. Each of the main synthetic base fluids is described for their chemical and physical properties, manufacture and production, their chemistry, key properties, applications and their implications when used in the environment.

2.1 Introduction

Synthetic lubricants have been available for many years; in the early 1930s, synthetic hydrocarbon and ester technologies were simultaneously developed in Germany and the United States. Development of a catalytic polymerisation process of olefins in the United States led to the formulation of automotive crankcase lubricants with improved low-temperature performance [1, 2]. These products were not commercialised due both to the inherent cost of these new synthetic base fluids and to performance improvements of mineral oil-based lubricants. In Germany, low-temperature performance drove the development of similar products [3], although the main objective was to overcome the general shortage of petroleum base stocks.

Other than the special supply circumstances of the Second World War, synthetic lubricants were not commercially significant until after the war. In general, the improved properties of lubricants achieved with early synthetic base stocks could be obtained more cost effectively by improved formulations based on mineral oils. But the requirement for lubricants to perform over increasing temperature ranges, led by military and aero-engine performance, stimulated continuing development of synthetic lubricant technology. Synthetic lubricants are now found in all areas of

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lubrication such as automobiles, trucks, marine diesels, transmissions and industrial lubricants, as well as aviation and aerospace lubricants.

Many compounds have been investigated as possible base stocks for synthetic lubricants, over 25 were identified in 1962 [3], of which seven types have major importance and are considered in this chapter:

- polyalphaolefins,
- alkylated aromatics,
- polybutenes,
- aliphatic diesters,
- polyolesters,
- polyalkylene glycols,
- phosphate esters.

Other important synthetic lubricant materials are the silicones, borate esters, perfluoroethers and polyphenylene ethers but these have restricted applications due either to high cost or to performance limitations and are not considered here. The recent development of pure hydrocarbon base fluids derived from gas-to-liquid, GTL, technology is also included in this chapter.

2.2 Polyalphaolefins

The term polyalphaolefin, PAO, when used for lubricant base stocks refers to hydrogenated oligomers of an α-olefin, usually α-decene. Several methods for the oligomerisation of α-olefins have been investigated for lubricant base stock production, the most important being free radical processes, Ziegler catalysis and cationic, Friedel–Crafts catalysis. After oligomerisation, the unsaturated products are separated from the reaction mixture, unwanted monomer removed and then the intermediate hydrogenated using supported nickel or palladium catalysts. Fractionation then gives the required viscosity grades, commonly 2, 4, 6 or 8 cSt at 100°C.

2.2.1 Free Radical Oligomerisation

Compared with other methods, very little work has been done on the free radical-initiated oligomerisation of α-olefins. This includes thermal oligomerisation of α-olefins, presumed to occur by a free radical process initiated by adventitious peroxide. The process has a high activation energy and gives low yields of poor-quality products [4]. The use of benzoyl peroxide or a di-*tertiary*-alkylperoxide allows oligomerisation to take place at lower temperatures than the thermal reaction. Oligomerisation of α-decene using di-*tertiary*-butylperoxide gave a product with rheological properties similar to the product of BF_3-catalysed oligomerisation [5].

However, in general, the free radical process is not amenable to controlling the degree of polymerisation and gives low product yields. The products of free radical oligomerisation tend to have poor viscosity/temperature characteristics due to skeletal isomerisation during the process.

2.2.2 *Ziegler-Catalysed Oligomerisation*

Ziegler catalysts studied for the oligomerisation of α-olefins tend to be based on modified first-generation catalysts, i.e. triethylaluminium/titanium tetrachloride. The aluminium/titanium ratio has a marked effect on product properties, at less than 0.8:1, liquids were produced, whereas at ratios above 1:1, waxy products were obtained [6, 7]. This effect is believed to relate to changes in the catalysis mechanism, from cationic to anionic with higher proportions of aluminium.

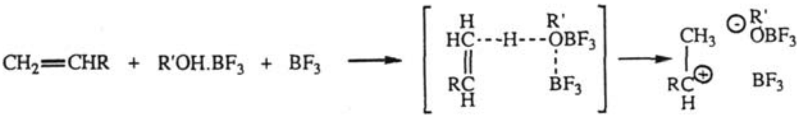
Standard Ziegler catalysts have the disadvantage of tending to give products with a broad distribution of oligomers. A propylene oxide-modified alkylaluminium/titanium tetrachloride catalyst produced a series of oligomers based on C_2 to C_{12} α-olefins, of which the C_8-based trimer was claimed to be an outstanding hydrocarbon fluid with a wide range of operating temperatures [8]. Other modified Ziegler systems are also capable of giving high yields of high-quality base stocks [9]; one example used an alkylaluminium halide/alkoxide zirconium halide catalyst [10], which controls the degree of oligomerisation of α-decene by changing the reaction temperature. Ziegler catalysts have been used to produce base stocks by co-oligomerisation of ethene with other α-olefins [11, 12]. A catalytic complex of di-isobutylaluminium chloride and di-ethoxychlorovanadate in the presence of hydrogen controlled the molecular weights of the reaction to give useful products.

2.2.3 *Friedel–Crafts-Catalysed Oligomerisation*

Although improvements to the Ziegler catalysts have been made, the requirement for a solvent, difficulties in handling, separation and recovery of the catalyst have led to the use of cationic Friedel–Crafts-type catalysts. These systems also tend to give higher monomer conversions, faster cycle times and greater control over oligomer distribution. The use of aluminium trichloride has been described for the polymerisation of α-olefins [1]. The reaction mechanism, Reaction (2.1), requires addition of a proton to the double bond, therefore a co-catalyst such as water is used [13–15].

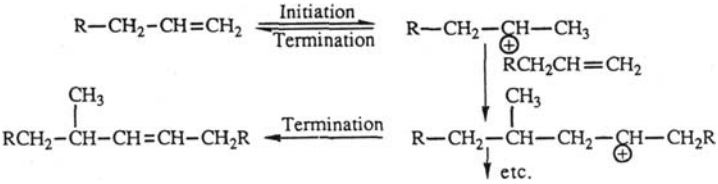
$$AlCl_3 + H_2O \rightarrow AlCl_3OH_2 \rightarrow (AlCl_3OH)^- + H^+ \qquad \text{(Reaction 2.1)}$$

Whilst such catalysts are very reactive, they can lead to cracking and isomerisation, which give products with complex structures and wide molecular weight distributions [16]. Oligomerisation can be controlled to some extent by using Lewis bases such as ethyl acetate or polyhydric alcohols in place of water as the co-catalyst [17]. Difficulty in controlling the oligomerisation process and the need for low-viscosity base fluids for automotive lubricants and aircraft hydraulic oils have led to the predominance of BF_3-based catalyst systems for α-olefin oligomerisation. As with $AlCl_3$, BF_3 requires a co-catalyst for effective oligomerisation; the type of co-catalyst such as water or an alcohol, acid, ether or ketone, has a significant effect on the degree of oligomerisation. The most common co-catalysts are alcohols, especially *n*-propanol and *n*-butanol. The co-catalyst is suggested as being needed in a less than molar equivalence to the Lewis acid [18], and an initiation step was proposed to account for this result, Reaction (2.2):



(Reaction 2.2)

A propagation step involving insertion of a monomer between the olefinic cation and its associated gegenion was proposed, Reaction (2.3), with termination occurring by proton transfer from the oligomeric cation [19]:



(Reaction 2.3)

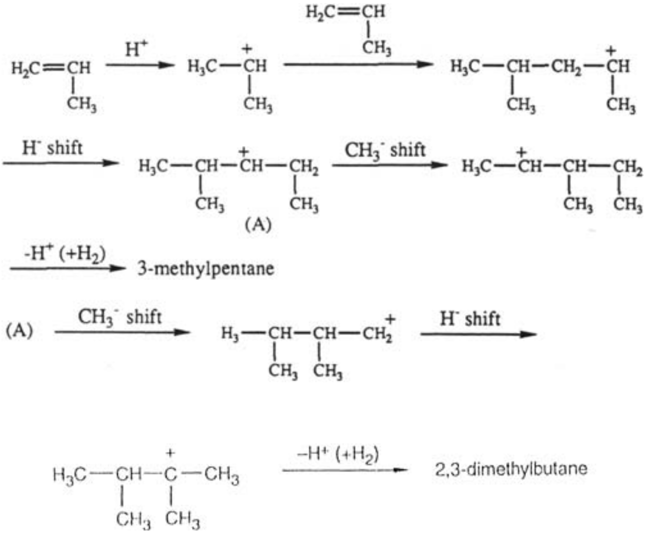
Whilst the BF_3-catalysed oligomerisation of α-olefins has many advantages over other methods through allowing control of the degree of oligomerisation, high conversions, lack of solvent and a short time cycle for the reaction, there is a problem in the inability to recycle the catalyst. The catalyst is normally removed by washing the reaction mixture with a solution of ammonia. A method of overcoming this problem by using a heterogeneous silica–BF_3–water catalyst, which allows the BF_3 to be easily recovered by distillation, has been proposed [20–23]. The BF_3-catalysed mechanism of α-olefin oligomerisation is not fully understood, in particular, the mechanism proposed in Reaction (2.3) does not account for the number of methyl groups in the products [19]. It has been postulated that methyl group migration in the dimer might explain the difference [24, 25]; however, the proposed mechanism requires the formation of an intermediate protonated cyclopropyl compound, which is energetically unfavourable.

Analysis of the monomer fraction product of an oligomerisation reaction has been considered as a route to understanding the reaction mechanism [18, 26, 27].

The high conversion polymerisation of α-decene gave a monomer fraction which contained 60% α-decene, 35% internal alkenes and 5% methylnonenes. The conclusion was that, in addition to methyl group migration, isomerisation of the double bond could also take place, even with the monomer. As polyalphaolefins derived from internal olefins usually give products with inferior temperature/viscosity properties, double bond isomerisation can be a problem.

Product analysis from long-chain alkene oligomerisation can be difficult, therefore low molecular weight alkene oligomerisation has been used as a model. Product analysis by infra-red from the oligomerisation of propene, but-1-ene and but-2-ene has identified the structural units [28]. Only internal alkenes were found and the structures obtained were believed to derive from intramolecular 1,2-hydride shifts and some tail-to-tail coupling of monomer units. Developments in ^{13}C NMR spectroscopy have allowed unambiguous assignments of chemical shifts in a number of hydrocarbon structures, allowing identification of specific structures within the hydrogenated dimer and trimer fractions of propene and butene polymerisations. This has led to the proposal of 1,2-hydride and methanide shifts, hydride transfer and proton elimination to explain the structure of the products [29, 30].

Gas chromatography–mass spectrometry analysis of the dimer and trimer fractions of the polymerisation products of propene and but-1-ene also suggested intramolecular hydride and methanide shifts as the source of the isomers formed. A mechanistic scheme for the oligomerisation of propene has been proposed, Reaction sequence (2.4) [31]. In most of the studies described above, the products have been analysed after hydrogenation. However, a study analysed the C_7 product of a propene/but-1-ene copolymerisation before hydrogenation and confirmed the role of hydride and methanide shifts in determining the structures of the products [32],



(Reaction sequence 2.4)

Analysis of the ‘simple’ structures obtained from the dimer and trimer fractions of short-chain alkenes showed the complexity of the oligomerisation reaction. It is not surprising that oligomerisation of the longer chain alkenes such as dec-1-ene should give complex mixtures of isomers. However, the rearrangements which give rise to the mixture of isomers are all intramolecular, thus giving products with predictable molecular weights.

Developments in PAO technology include using acidic aluminosilicate shape-selective catalysts. Use of chromium on silica gel catalyst and a shape-selective metallosilicate produced olefin oligomers as suitable intermediates for reaction with an enophile to produce polar synthetic base stocks [33].

2.2.4 Properties and Applications

The complexity of the oligomerisation mechanism of dec-1-ene leads to one of the important properties of PAOs as lubricant base fluids. The higher than expected degree of branching in the final product gives very good low-temperature properties, especially as the products are wax-free. In addition, the molecular rearrangements are intramolecular and molecular weights are therefore predictable. Thus, PAO volatilities are lower than those of equiviscous mineral-derived products, whether solvent refined, hydrocracked or hydroisomerised. Overall, the PAOs are able to operate effectively over a very wide temperature range. Table 2.1 compares typical viscosities at 100°C, pour points and volatilities for solvent-refined SN 150, hydroisomerised and PAO base fluids.

Table 2.1 Base fluid comparisons

Physical property	SN 150	Hydroisomerised	PAO
Viscosity at 100°C (cSt)	5.43	5.64	5.98
Pour point (°C)	−12	−15	−64
NOACK (% loss)	15	7.8	6.1

In addition to controlling temperature/viscosity properties to give base oils with low pour points and high viscosity indices, the oligomerisation process also gives high-purity base fluids. These can be used to formulate lubricants with very good thermal and oxidative stability. Interestingly, in some oxidation tests on base oils without additives, mineral base oils appear to be superior to PAOs, e.g. the onset of oxidation measured by differential scanning calorimetry, DSC. This is ascribed to naturally occurring antioxidants present in mineral oils which survive the refining process. However, PAOs are more responsive to added antioxidants which leads to the superiority of fully formulated lubricants based on PAOs [34].

The composition purity of PAOs, and their low polarity, gives poor solvency for polar compounds such as the additives required for fully formulated engine lubricants. The very low polarity can also cause problems with seal performance. Therefore, PAO base fluids tend to be combined with other, more polar base fluids such as aliphatic esters (as synthetic lubricants) and solvent-refined mineral oils (as part-synthetic lubricants).

The wide temperature performance range for PAO-based lubricants together with their excellent physical, chemical and thermo-oxidative stabilities has increased the use of PAOs in a wide variety of applications. Traditional application areas such as aerospace, transmissions and hydraulic systems continue to require the lubricant performance benefits of PAOs. In addition, the stresses of both increased performance and longer lifetimes placed on automotive and marine lubricants have increased growth in the use of PAO-based synthetic lubricants in these applications.

2.3 Base Oils from Natural Gas Using ‘Gas-to-Liquids Technology’, GTL

2.3.1 Introduction

Natural gas, the most volatile fraction of crude petroleum, is usually associated with oil-producing wells as a by-product – often unwanted. The gaseous components associated with crude petroleum vary with the individual production oil field but a very broad description of the composition of natural gas is given in Table 2.2.

Table 2.2 Composition of natural gas

Gaseous component	Chemical formula	Percentage composition
Methane	CH_4	85–95
Ethane, propane, butane	C_2H_6–C_4H_{10}	2–10
Carbon dioxide	CO_2	0–10
Nitrogen	N_2	1–5
Hydrogen sulphide	H_2S	0–5

The proportion of natural gas in a petroleum reservoir is related to the reservoir formation temperature, with higher temperatures leading to higher gas concentrations. Some reservoirs contain mainly natural gas, in some cases as nearly pure methane. Methane is a very effective energy source with environmental benefits especially in reducing combustion-derived emissions as it is the cleanest burning hydrocarbon. However, transportation and storage can be difficult and expensive especially when gas reservoirs are in isolated places. The most effective transportation method is by pipeline but for remote reservoirs the capital cost of installing a pipeline to bring gas to potential users becomes prohibitive. The gas can be transported as liquefied natural gas, LNG, but there are significant infrastructure costs associated with specialised tankers, the energy requirements of liquefaction at source, keeping the LNG refrigerated in transit and re-gasification facilities at the delivery point. Conversion of LNG into higher molecular weight liquid hydrocarbons at the gas source allows use of the existing oil distribution infrastructure of tankers, pipelines and storage facilities.

GTL technology has been under development for many years but, except for some earlier special cases in South Africa and Germany, significant commercial developments have taken place since the 1990s. The driving forces of the more recent developments include recognition of the need to exploit remote gas reserves, the need for cleaner burning fuels to meet emissions legislation and developments in GTL technology that have improved conversion efficiencies and reduced costs. Whilst the primary focus for GTL is on fuels, lubricant base stocks have been produced commercially (Shell Middle Distillate Synthesis in Malaysia) and more developments are planned that include the production of lubricant base stocks [35].

2.3.2 Gas-to-Liquids Technology

Production of lubricant base stocks from natural gas requires three steps:

- syngas formation, a mixture of carbon monoxide and hydrogen,
- production of waxy hydrocarbons from syngas by a Fischer–Tropsch synthesis,
- final product manufacture.

Depending on the purity of the gas feedstock, there may be pre-treatment of natural gas to remove impurities such as sulphur compounds that will poison catalysts used in subsequent processes. There are three common technologies in use to convert natural gas into syngas: steam methane reforming (SMR), partial oxidation (POX) and auto-thermal reforming (ATR).

Syngas production – steam methane reforming, SMR: Steam and natural gas are reacted at high temperature (800–1000°C) and moderate pressure (20–30 bar) over a nickel catalyst supported on alumina to give Reaction sequence (2.5):

$$\begin{aligned} CH_4 + H_2O &= 3H_2 + CO \\ CO + H_2O &= H_2 + CO_2 \\ CH_4 + CO_2 &= 2H_2 + 2CO \end{aligned} \qquad \text{(Reaction sequence 2.5)}$$

The second reaction, the water shift reaction, is slightly exothermic and always occurs in SMR, the other reactions are endothermic. The main disadvantage of the SMR process is that it tends to produce syngas with too high a ratio of hydrogen to carbon monoxide for the subsequent Fischer–Tropsch synthesis. This is overcome by removing the excess hydrogen and/or by using natural gas with a high carbon dioxide content. The key advantage of the SMR process compared with the others is that oxygen or oxygen-enriched air is not needed, only steam.

Partial oxidation, POX: Methane is partially combusted at high temperatures, 1200–1500°C, under pressure, 140 bar, in the absence of a catalyst, Reaction (2.6):

$$2CH_4 + O_2 = 4H_2 + 2CO \qquad \text{(Reaction 2.6)}$$

The hydrogen/carbon monoxide ratio is nearly ideal for the Fischer–Tropsch stage. However, extra oxygen is needed and the high reaction temperatures lead to unwanted by-products such as soot and ammonia, so the syngas has to be chemically scrubbed.

Auto-thermal reforming, ATR: This process combines elements of both SMR and POX as it uses a catalyst to produce syngas from natural gas in the presence of both steam and oxygen, Reaction (2.7):

$$2CH_4 + H_2O + \tfrac{1}{2}\,O_2 = 5H_2 + 2CO \qquad \text{(Reaction 2.7)}$$

The temperatures are not as high as in the POX process, ~1000°C, which, together with the use of steam, leads to fewer unwanted by-products such as soot and ammonia being generated. The hydrogen/carbon monoxide ratio is somewhat high for the Fischer–Tropsch stage but can be adjusted by changing the steam/gas ratio. One modified ATR process uses air rather than oxygen. Other technology developments include the use of ceramic membranes to separate oxygen from air as a more cost-effective air separation process.

Fischer–Tropsch synthesis: Syngas is converted into linear hydrocarbons in a Fischer–Tropsch synthesis. Iron and cobalt catalysts can be used with or without co-catalysts on a support such as alumina, silica or titania. The real reaction system is much more complex than Reaction (2.8), with side reactions producing olefins and alcohols as well as others. A simplistic reaction description is as follows:

$$n\mathrm{CO} + (2n + 1)\mathrm{H}_2 = \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O} \qquad \text{(Reaction 2.8)}$$

There are two generic Fischer–Tropsch processes: one operating at high temperatures of 300–350°C, HTFT, and one at lower temperatures of 200–250°C, LTFT. The HTFT process uses iron-based catalysts and tends to produce relatively low molecular weight species that include olefins and significant levels of oxygenates. The LTFT process uses either iron- or cobalt-based catalysts and produces high levels of waxy paraffins. The catalyst of choice tends to be based on cobalt due to its stability, long life and high activity, although it is more costly.

However, the high activity together with the exothermic reaction makes reactor design critically important to ensure effective heat removal. Tubular fixed bed reactors (TFBR) are particularly vulnerable to thermal damage, so tube diameters are limited to prevent heat transfer problems. This leads to an expensive reactor as a large number of small tubes have to be used.

One preferred process uses a slurry phase reactor, SPR, as this allows for very good heat transfer and temperature control. The syngas is introduced at the bottom of a reactor containing a catalyst slurry in a high boiling paraffin. The syngas components diffuse through the liquid phase to the catalyst particles. The higher molecular weight products now form part of the slurry, whilst any lighter by-products pass through the reactor. Whilst the reactor is simpler in design than a TFBR, it is important that there should be no stagnant zones with poor mixing that could lead to local high temperatures. Another key design criterion is to have an efficient process to separate the catalyst from the waxy products. Recent process developments have centred on improving catalyst performance by maximising its surface area and increasing catalyst robustness during the separation of product from catalyst.

One of the advantages of a TFBR is the ease with which the product separates from the catalyst: the liquid waxes simply flow out of the catalyst bed. Also, if the reactor becomes contaminated with sulphur compounds, only the part of the catalyst bed closest to the reactant entrance will be de-activated, whereas with the SPR then, all the catalyst will be susceptible to poisoning. This disadvantage can be overcome by ensuring that sulphur removal processes for the syngas feedstock are wholly efficient. However, in contrast, there are a number of advantages of SPRs over TFBRs, which are as follows:

– reduced reactor cost,
– reduced pressure drop leading to reduced gas compression costs,
– reduced overall complexity and maintenance costs,
– increased flexibility of operating conditions.

Wax isomerisation: In principle, any of the existing processes for upgrading crude oil fractions such as hydrocracking, hydrotreatment and isomerisation can be used to convert the waxy hydrocarbons into useful base oils. Mild hydrotreatment can be useful for converting any olefins and alcohols but the preferred process makes use of isomerisation as hydrocracking tends to be used to produce GTL diesel fuel. The iso-de-waxing process described previously in Section 1.5.5 is particularly effective as is also the Shell Middle Distillate Synthesis process that combines hydrocracking and isomerisation over a dual-function catalyst. Typical conditions use a platinum catalyst on an alumina–silica support with a pressure of 30 bar and temperature of 350°C [35].

2.3.3 Product Properties

As described in Section 1.6, the quality of lubricant base oils is categorised by the American Petroleum Institute and the latest categories are described in API 1509 (API 2007) [36]. Group IV base stocks are polyalphaolefins (PAO) and Group V base stocks include all other base stocks not included in Group I, II, III or IV. GTL base oils are in the Group III+ category, with typical viscosities at 100°C of 4–6 cSt. They are also very pure with zero sulphur, nitrogen, aromatics and olefins.

Traditionally, synthetic PAOs have had significant performance advantages over equiviscous mineral base oils by their higher viscosity index, lower pour point, reduced volatility and improved oxidation stability in the presence of antioxidants. GTL base oils now challenge PAOs in performance and can be very cost competitive with the relatively expensive synthetics. A review in 2006 described performance comparisons of base oils with a viscosity of 4 cSt at 100°C [37]. It is suggested that the GTL fluids can match the PAOs in Noack volatility, oxidation resistance and thermal stability, whereas the PAOs retain some superiority in their extreme low-temperature fluidity.

2.4 Alkylated Aromatics

2.4.1 Introduction

Three types of alkyl benzenes are available for use as, or in, lubricants: (i) the dialkyl benzenes produced as a by-product in the manufacture of linear dodecyl benzenes or tridecyl benzene, a sulphonation feedstock for anionic detergent manufacture, (ii) the dialkyl benzenes produced from these detergent alkylates by reacting further with α-olefins; and (iii) synthesised alkyl aromatics purpose-built from benzene and short-chain olefins such as propylene. Characteristics of these oils which either individually or in combination make them suitable for particular applications include sulphur-free chemistry, low pour point, good thermal stability compared with mineral oils and good solvency. Furthermore, sulphonated alkyl aromatics, particularly those derived from the purpose-made materials, as in type (iii) above, are used as emulsifiers in metalworking fluids as the sodium salts and as detergents in automotive crankcase lubricants as the calcium and magnesium salts.

2.4.2 Production and General Properties

The lowest cost (di)alkyl benzenes are by-products from linear monoalkylate manufacture used extensively in detergent manufacture. Synthesis is usually by a Friedel–Crafts-type reaction, either by reaction of the alkyl chloride and benzene with anhydrous aluminium chloride as catalyst, or by the catalysed reaction of the appropriate length α-olefin and benzene.

The more specialised alkyl benzenes are synthesised from benzene and propylene, with catalysts and conditions selected to give some control over the molecular weight and structure, and therefore physical and chemical properties, of the alkyl component. Properties of synthetic alkyl benzenes vary widely depending on the chemical type and are therefore difficult to generalise. However, a typical structure is shown in Fig. 2.1, a typical value of x would be 3, giving a viscosity of 4 cSt at 100°C and a viscosity index of 100. With this structure, pour points of –40°C are attainable as the material is essentially wax-free. The presence of the aromatic ring gives a fairly high degree of polarisability to the molecule, resulting in good solvating powers for most lubricant additives.

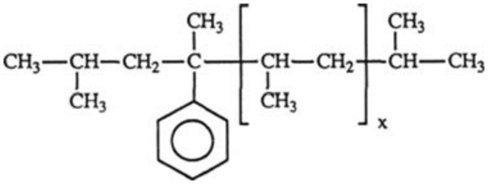


Fig. 2.1 Synthetic alkyl benzene

2.4.3 Applications

The lower cost dialkyl benzenes are used in a wide variety of industrial and metalworking products. In particular, their sulphur-free chemistry has led to extensive use as rolling and drawing oils for copper. The synthesised alkyl benzenes, even when their chemistry is optimised, generally exhibit poorer properties than PAOs. However, their excellent solvency and low pour point make them suitable for lubricants designed for extremely low-temperature operations in arctic greases, gear oils, hydraulic and power transmission fluids.

The most widespread use of the tailored alkylates is, however, as refrigerator oils. When carefully designed, the oils are fully compatible with fluorinated refrigerants such as R22 and R502, whereas mineral oils suffer from wax precipitation and PAOs give phasing problems. The oil may be carried through the entire refrigeration circuit, experiencing extremes of temperature and so good thermal stability is therefore essential. The natural solvency of the alkylates is also beneficial in minimising the formation of sludge, varnishes and other deposits. Normally, no supplementary additives are required but in applications where operating conditions are particularly severe, anti-wear compounds such as triaryl phosphates have been successfully used.

Another, quite different, application of the lower molecular weight alkyl benzenes, C_9 to C_{16}, either neat or blended with mineral oils, is as transformer oils, where an exceptionally high resistance to gas evolution is required.

2.5 Polybutenes

2.5.1 Introduction

Polybutenes used in lubricants are mainly composed of isobutene and often referred to as polyisobutenes, or ‘PIBs’. Compared with polyolefin fluids of equal viscosity, polybutenes have different physical properties from PAOs, which are usually synthesised from higher molecular weight, straight-chain, α-olefins. The low molecular weight polybutenes are used where their ability to depolymerise and burn completely without leaving deposits is advantageous. Being hydrocarbons, polybutenes are compatible with mineral oils on the ‘like dissolves like’ principle with good metal wetting properties and improved film strength. Polybutenes have a very wide range and variety of applications; in lubricant applications [38], they are used as viscosity index improvers, VIIs, as base fluids themselves and also in dispersant synthesis, e.g. as PIB succinimides, Chapter 7.

2.5.2 Production

Polybutenes are produced by polymerisation of a hydrocarbon stream containing isobutene, other butene olefins (butene-1 and butene-2) and butanes. The main sources of the C_4 feedstock are naphtha steam and refinery catalytic cracker operations [39]. A Lewis acid-catalysed polymerisation gives an isobutene/butene copolymer with the polymer backbone built up predominantly of the isobutene monomer repeat unit. The higher molecular weight polymers contain very low levels of other butene structures and have a regular dimethyl branch, derived from the isobutene monomer unit, every other carbon atom down the polymer chain. Higher levels of other butene structures are found in the lower molecular weight polymers, which consequently have a more complex structure. Independent of molecular weight, these copolymers are all commonly referred to as polybutenes and by the trivial, if scientifically incorrect, abbreviation PIBs.

The polybutene structure also contains one carbon–carbon double bond at the end of the polymer chain [40]. The nature of this double bond is important in defining the ease with which it will undergo chemical modification. Normally it is found as the *cis*- and *trans*-trisubstituted group, but polybutenes having the more reactive disubstituted vinylidene structure are now available, Fig. 2.2. Polybutenes have good stability as lubricant components, even whilst containing the residual unsaturation. It is possible to react the double bond to produce products such as lubricant dispersants, see Chapter 7, but the reaction is achieved only under certain controlled conditions.

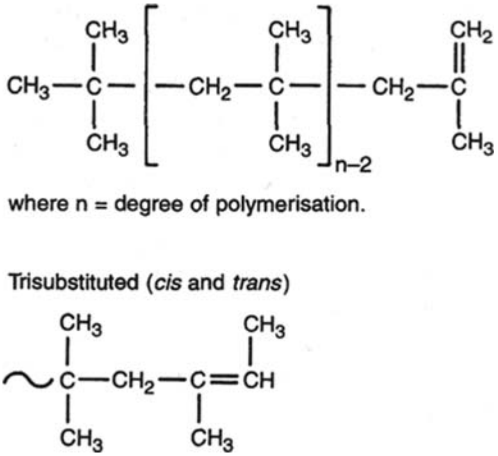


Fig. 2.2 Polybutene structures

By modifying the temperature of the polymerisation it is possible to produce polybutenes with molecular weights of 260 up to 6000 amu, which range in viscosity from free-flowing oils to tacky, semi-solid rubbers. Polybutenes are polymers which are liquid in character at ambient temperatures, with even the most viscous grades subject to flow if given sufficient time. Higher molecular weight polymers can be obtained by the polymerisation of a feed stream containing isobutene as the only polymerisable monomer. The resulting polyisobutenes, correctly referred to as PIBs, are rubbers and have molecular weights ranging from 10,000 to several million.

2.5.3 Markets

Polybutene is an extremely versatile material and used either in a derivatised form as oil and gasoline additives or in applications using its physical properties. Worldwide production of polybutene is estimated at around 650 kt/Pa, of which about 60–70% is derivatised to polybutenyl succinimide for use as dispersant additives to combat sludge in crankcase engine oils and as detergent additives in gasoline to prevent carburettor fouling and engine deposits. Between 5 and 10% of polybutene is used in cable applications for impregnating paper used for power cables and as non-draining, filling compounds to guard against water penetration of telecommunication and fibre optic cables. Industrial applications at 20–25% of total production exploit the physical properties of polybutene. Polybutenes are widely used in oils and lubricants, adhesives and sealants, tackified polyethylene, bitumen and rubber modification, concrete mould oils and in putties, anticorrosion coatings, masonry coatings, paints, inks and dispersion aids. It is estimated that 30% of polybutene sold for industrial application is for oils and lubricants.

2.5.4 Properties

Polybutenes are non-polar and soluble in aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons and certain oxygenated solvents such as tetrahydrofuran and diethyl ether. They are insoluble in simple alcohols, esters and ketones. In lubricant applications, polybutenes are normally combined with other base fluids and compatibility is found with all types of mineral oils, polyalphaolefins (PAOs), alkyl benzenes and most types of synthetic esters. Incompatibility is found with polyalkylene glycols and, with few exceptions, silicone oils. Fluoroelastomers, polychloroprene and nitrile rubbers are unaffected by polybutenes and are most suitable for pump seals and packings in handling equipment. Grades of polybutene are defined by the viscosity measured in SSU (Saybolt viscosity) at 100°C divided by 100 or by direct reference to molecular weight. Grades representative of the range of polybutenes available commercially are shown in Table 2.3 and a summary of the properties of polybutene relating to their use in oils and lubricants is shown in Table 2.4.

2.5.5 Lubricant Applications

Compared on an equal viscosity basis, the properties of a polybutene, a PAO and an ester, the polybutene is more volatile, less resistant to oxidation and has a lower viscosity index. This illustrates the limitations of polybutene as a true synthetic base oil. For example, it would be inappropriate to use a low-viscosity polybutene as the base oil for crankcase engine oils. Polybutenes are used as a major base fluid for

Table 2.3 Typical properties of commercially available polybutenes[a]

			Polybutene grade[b]										
Property	Unit	Method	O3	O4	O7	3	5	10	30	150	200	600	2000
Molecular weight	Mn	ASTM 5296	260	310	440	620	780	950	1250	2300	2600	4200	5900
Viscosity at 100°C	cSt	ASTM D445	2	3.4	13	55	103	225	635	3065	4250	12200	40500
Viscosity at 100°C	SSU	ASTM D445	32	39	70	270	480	1050	2960	14300	20000	57000	190000
Flash point, PMCC	°C	ASTM D93	105	120	130	140	155	165	170	175	175	180	190
Flash point, COC	°C	ASTM D92	110	135	145	155	190	210	240	250	270	275	280
Pour point	°C	IP 15/86	−60	−60	−30	−21	−12	−7	4	18	24	35	50
Relative density	20°C	IP 90/86	0.815	0.833	0.852	0.874	0.882	0.891	0.895	0.904	0.910	0.914	0.917
Viscosity at 40°C	cSt	ASTM 445	6.6	15	126	1090	2900	7200	21000	133000	185000	620000	180000
Viscosity index		ASTM2270	92	92	95	98	100	125	181	246	264	306	378
Refractive index		ASTM1747	1.461	1.467	1.474	1.487	1.490	1.494	1.498	1.503	1.504	1.505	1.508
Bromine number	gBr/100 g	IP 129/87	–	–	40	27	20	16	12	8	6	4	3

All grades have a colour value (Hazen) of 20, by ASTM D1209, an acid number (AN) of 0.03, by ASTM D974, a water content, ppm, of 40, by ASTM1744, and a Conradsen residue (percentage residue) of < 0.01, by ASTM D189.

[a] Data from BP Chermicals Publications.

[b] The approximate grade number, from division of SSU viscosity at 100°C (line 3) by 100.

Table 2.4 Polybutene properties for oil and lubricant applications

Wide range of polybutene grades available
Viscous grades have high viscosity index
All grades depolymerise at elevated temperatures, leaving no residue
Stable to UV radiation and under less severe conditions to oxidative degradation
Medium- and high-viscosity grades provide tackiness and adhesiveness
Colourless
Hydrophobic
Practically non-toxic
Good lubricants

two-stroke oils, high-pressure polyethylene compressor lubricants, metalworking lubricants and speciality greases. In these applications the prime requirement is for low smoke, low deposits or low toxicity, with volatility and oxidation resistance being less critical. At lower treat levels, the more viscous grades of polybutene are used in viscosity adjustment and viscosity index improvement and to provide adhesiveness, tackiness and resilience for greases and energy-efficient automotive and industrial oils [41]. The key benefits that polybutene provides in its major areas of application are shown in Table 2.5 and the main grades of interest for use in each of the lubricant sectors are summarised in Table 2.6. In Fig. 2.3 the change in viscosity with temperature is plotted for a range of polybutenes. The following sections review the main lubricant applications for polybutene in brief.

Table 2.5 Polybutene: key properties for lubricant sectors

Application	Key property
General	Control of viscosity
Two-stroke lubricant	Low smoke, low blocking, good lubricity, clean burning
Metalworking fluid	Non-staining, low deposits, low toxicity, low biodegradability
Gear oil	Shear stable, viscosity index improver, adhesiveness additive
Compressor lubricant	Good lubricity, inertness, low toxicity, good electrical properties
Grease/wire rope	Adhesiveness, hydrophobic, inertness, good lubricity

Table 2.6 Polybutene grades of interest for use in oils and lubricants

Application	03	04	07	3	5	10	30	150	200	600	2000
Viscosity Adjustment						X	X	X	X	X	X
Two-stroke oils	X	X	X	X	X	X	X				
Metal-working lubricants		X	X				X	X	X		
LDPE compressor					X		X	X	X		
Gear/Hydraulic oils					X		X	X	X	X	X
Greases	X	X		X		X	X			X	X
Wire rope protectives						X	X				X

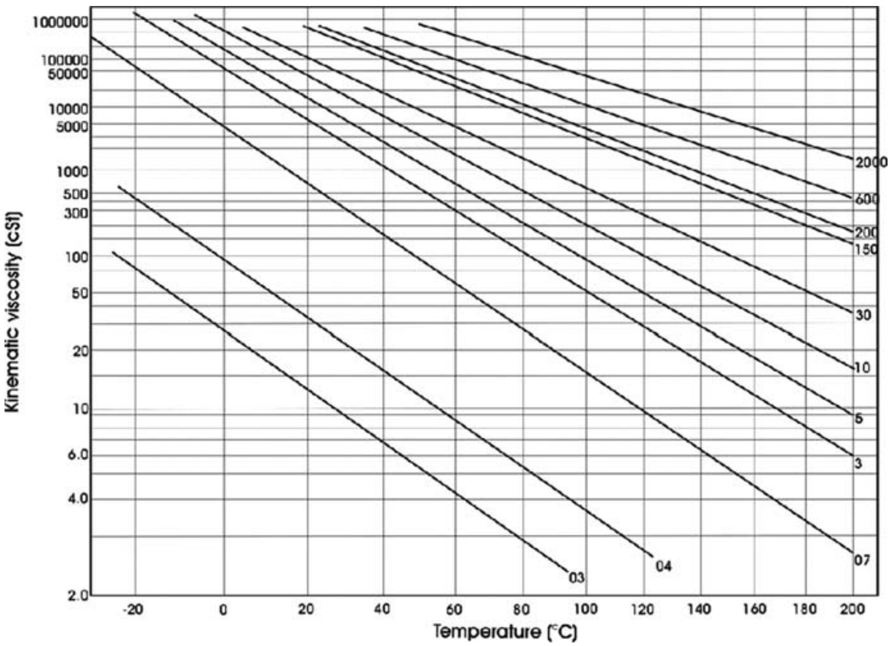


Fig. 2.3 Change in viscosity with temperature for various polybutenes

Two-stroke oils: Global performance specifications have been introduced for two-stroke oils to assure the modern image of the two-stroke engine and to allow for continued improvements in engine performance. Engine manufacturers, working with JASO (Japan Automobile Standards Organisation), have responded to growing environmental pressure with specifications to reduce smoke emission from exhaust systems together with a standardisation of worldwide lubricant quality [42]. Specifications cover lubricants used in motorcycles, scooters, chainsaws, snowmobiles and agricultural equipment. They benchmark lubricant performance in terms of lubricity, initial torque, visible smoke, exhaust system blocking and detergency. Polybutenes' ability to depolymerise cleanly at temperatures found in the two-stroke engine plays a central role to meet the smoke and blocking requirements of the major oil types specified by engine manufacturers [43–46]. Polybutene levels of 30% formulated with mineral oil, hydrocarbon diluent and additive package are typically required to meet the minimum quality of JASO FC and Global GC/GD oils. Formulations with polybutene levels up to 55% or formulations combining polybutene and synthetic ester are options for further increasing modern two-stroke lubricant performance. Polybutenes are not classed as biodegradable and synthetic esters are chosen to meet requirements of biodegradability required for some outboard two-stroke lubricants.

Metalworking Lubricants: Polybutenes provide a practically non-toxic base oil that gives non-staining and low deposit-forming characteristics to metalworking lubricants for processing aluminium, steel and copper. During annealing or heat treatment, any polybutene lubricant remaining on the metal surface rapidly and completely depolymerises to leave the surface free of stains or deposits. This behaviour contrasts with that of mineral oil lubricants which can leave deposits on the metal following exposure to high temperatures. The aluminium industry is a major user of polybutene lubricants, used extensively in aluminium forming processes and as components of bearing lubricants and hydraulic oils for aluminium mills where non-staining and low toxicity are essential requirements. Stable emulsions of polybutene are used for high-temperature metal-cutting applications. Polybutenes are more resistant to biodegradation than mineral oils and their emulsions are less susceptible to microbial attack and therefore increased service life of metalworking fluids containing them.

Automotive and industrial gear oils: Multi-grade oils give improvements in low-temperature performance and cold starting and therefore improvements in fuel economy. Polybutenes are shear-stable polymers used as viscosity index improvers in the formulation of high-quality, multi-grade or energy-efficient automotive and industrial gear oils. Polybutenes can be combined with mineral oils to meet SAE 80W/140 specification for commercial vehicles and combination with special base oils will help meet the SAE 75W/90 specification for automobiles. They are also used to achieve industrial gear oil specifications, particularly the higher viscosity specifications, where if incorporated at levels of 15–25% give benefits in adhesion, low deposit formation and energy efficiency.

Compressor lubricants: As an example, low-density polyethylene, LDPE, is manufactured by a high-pressure autoclave or tubular process. A secondary compressor barrel is used to generate the high pressures of ethene gas required for the free radical polymerisation. Polybutenes perform well in lubrication and sealing duties and meet the special requirements of high purity, low deposit formation, inertness and food contact approval for this application. Polybutene grades are used alone or in combination with other special oils and find use where the electrical or coating properties of the low-density polyethylene must be assured [47]. Polybutenes are also used for the lubrication of the secondary compressor barrel in the manufacture of ethylene–vinyl acetate copolymer by the high-pressure production process.

Greases: The low toxicity, high viscosity index and adhesive qualities of polybutenes improve the properties of base oils used in the manufacture of high-performance greases for automotive, industrial and specialist application. Grease manufactured from a base oil consisting of polybutene and mineral oil shows improvements such as better viscosity/temperature performance, adhesive and cohesive strength, reduced oil bleeding and water washout, increased service life and improved performance at low temperatures. Polybutenes are also used in high-temperature speciality greases as carriers for solid lubricant suspensions such as graphite and molybdenum disulphide. These types of lubricants are normally used on conveyor chains and roller bearings or used as release agents in the steel and glass industries. Again, polybutenes contrast with mineral oil products in not forming deposits on their high-temperature thermal decomposition and prevent problems of wear, seizure and corrosion.

Wire rope protectives: Wire ropes require a lubricant which reduces wear between wires and strands when flexing. Polybutene meets the requirements of a wire rope lubricant by providing inertness, adhesion, corrosion prevention and lubricity. Using either a high-viscosity polybutene in combination with a suitable base oil or a lower viscosity grade with a gelling agent controls the viscosity and drop point of the protective lubricant to suit each application. Concern for the health, safety and technical performance of traditional wire rope protectives based on bitumen has resulted in a move to safer and higher performance products based on polybutene. The same properties that make polybutene a good wire rope protective have also led to its use in high-performance, anticorrosion coatings for metals in transit or storage and in protective coatings for automobiles. Protective films containing 30–40% polybutene prevent the formation of gums and staining on the metal which can occur if the protective is mineral oil based.

Synthetic lubricants: Polybutenes can be combined with esters and polyalphaolefins to provide high-performance, full synthetic blends benefiting from the properties shown in Table 2.5. In particular, the use of polybutene gives the formulator excellent opportunities to combine lubricant viscosity control with properties of low deposit formation, clean burning and tackiness. Lubricant formulations combining polybutene and ester are used in high-performance, two-stroke lubricants, industrial oils, grease and chain lubricants. Blends of the more viscous polybutene grades and PAO give a useful increase of the blend viscosity index and are used in greases and industrial oil applications.

2.5.6 Conclusions and Future

Polybutenes combine effective viscosity control with the ability to deliver a number of key benefits and performance characteristics to an extensive range of automotive and industrial lubricants. Limitations in volatility and oxidation resistance limit the use of low-viscosity polybutenes in some of the more traditional base oil applications.

Demand for polybutene is expected to increase for use in clean burning two-stroke oils to meet new global emission and performance requirements. Demand is also expected to increase for specialist metalworking lubricants, grease and energy-efficient oils. With lubricants under greater scrutiny for evidence of hazard, formulators require the use of safe, non-hazardous and cost-effective components for lubricants. These requirements should cause synthetic oils such as polybutene to play a greater role in the future lubricant formulations. Combination of polybutenes with esters and PAOs is expected to grow in the future with formulators using the advantage of combinations of synthetic oils to achieve a synergistic response from base oil blends.

2.6 Synthetic Esters

2.6.1 Introduction

Prior to the early 19th century, the main lubricants were natural esters contained in animal fats such as sperm oil and lard oil, or in vegetable oils such as rapeseed and castor oil. During the Second World War, a range of synthetic oils was developed, amongst which esters of long-chain alcohols and acids proved to be excellent as low-temperature lubricants. Following the Second World War, further development of esters was closely linked to that of the aviation gas turbine. Neopolyol esters were used in the early 1960s for this application because of their low volatility, high flash points and good thermal stabilities. Esters are now used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and grease formulations. The inherent biodegradability of ester molecules gives added benefits.

2.6.2 Ester Types

The direct effect of the ester group on the physical properties of a lubricant is to lower volatility and raise flash point, due to strong dipole moments called London forces, binding the lubricant together. The presence of the ester group also affects other properties, discussed more fully later in the chapter, such as:

- thermal stability,
- hydrolytic stability,
- solvency,
- lubricity,
- biodegradability.

The major types of esters and their feedstocks are reviewed in Table 2.7 and Table 2.8 summarises their physical properties.

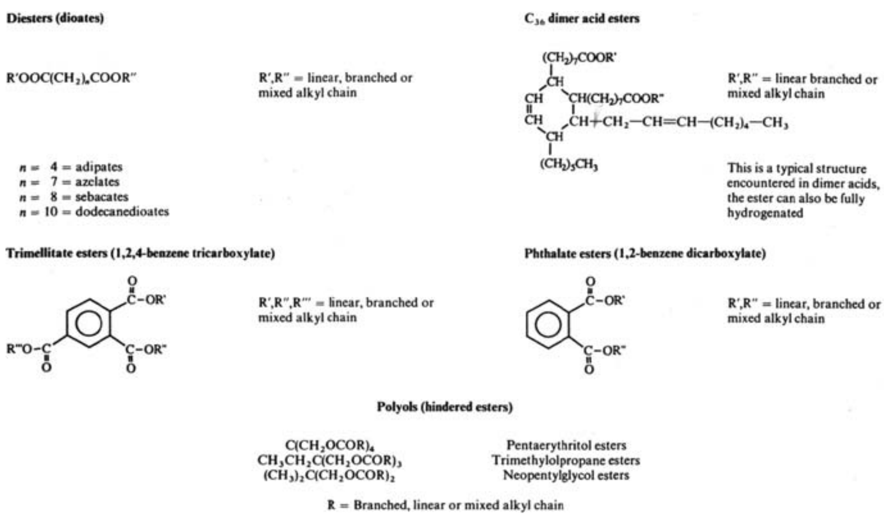
2.6.3 Manufacture of Esters

Ester production consists of three distinct processes: esterification, filtration and distillation. The simplistic, fundamental reaction is that of Reaction (2.9):

$$\text{acid} + \text{alcohol} \rightarrow \text{ester} + \text{water} \qquad \text{(Reaction 2.9)}$$

which is reversible but driven to completion by using excess alcohol and removing water as it is formed. An azeotropic agent such as toluene to remove water can be used.

Table 2.7 Ester types



Diesters (dioates)

$R'OOC(CH_2)_nCOOR''$

R',R'' = linear, branched or mixed alkyl chain

n = 4 = adipates
n = 7 = azelates
n = 8 = sebacates
n = 10 = dodecanedioates

C_{36} dimer acid esters

R',R'' = linear branched or mixed alkyl chain

This is a typical structure encountered in dimer acids, the ester can also be fully hydrogenated

Trimellitate esters (1,2,4-benzene tricarboxylate)

R',R'',R''' = linear, branched or mixed alkyl chain

Phthalate esters (1,2-benzene dicarboxylate)

R',R'' = linear, branched or mixed alkyl chain

Polyols (hindered esters)

$C(CH_2OCOR)_4$	Pentaerythritol esters
$CH_3CH_2C(CH_2OCOR)_3$	Trimethylolpropane esters
$(CH_3)_2C(CH_2OCOR)_2$	Neopentylglycol esters

R = Branched, linear or mixed alkyl chain

Table 2.8 Summary of ester properties

	Diesters	Phthalates	Trimellitates	C35 dimer esters	Polyols	Polyoleates
Viscosity at 40°C	6–46	29–84	47–366	90–185	14–35	8–95
Viscosity at 100°C	2–8	4–9	7–22	13–20	3–6	10–15
Viscosity index	90–170	40–90	60–120	120–150	120–130	130–180
Pour point (°C)	–70 to –40	–50 to –30	–55 to –25	–50 to –15	–60 to –9	–40 to –5
Flash points	200/260	200/270	270/300	240/310	250/310	220/380
Thermal stability	Good	Very good	Very good	Very good	Excellent	Fair
Conradson carbon	0.01/0.06	0.0/0.03	0.01/0.40	0.20/0.70	0.01/0.10	?
Percentage biodegradeable	75–100	46–88	0–69	18–78	90–100	80–100
Costs (PAO = 1)	0.9–2.5	0.5–1.0	1.5–2.0	1.2–2.5	2.0–2.5	0.6–1.5

The acid and alcohol are reacted thermally, usually with a catalyst in an esterification reactor with typical conditions of 230°C and 50–760 mmHg pressure. Significant amounts of alcohol vaporise together with water and must be recovered, accomplished by condensing the reactor vapours, separating the resulting two-phase liquid mixture and returning the alcohol to the reactor. Catalysts used include sulphuric acid, *p*-toluene sulphonic acid, tetra-alkyl titanate, anhydrous sodium hydrogen sulphate, phosphorus oxides and stannous octanoate. After the ester has been formed, unreacted acid is neutralised using sodium carbonate or calcium hydroxide and removed by filtration.

Polyol esters are made by reacting a polyhydric alcohol, such as neopentyl glycol (NPG), trimethylol propane (TMP) or pentaerythritol (PE), with a monobasic acid to give the desired ester. When making neopolyol esters, excess acid is used because the acid is more volatile than the neopolyol glycol and therefore easier to recover from the ester product.

2.6.4 Physicochemical Properties of Ester Lubricants

As described in Chapter 1, mineral oil base stocks are derived from crude oil and are complex mixtures of naturally occurring hydrocarbons. Synthetic ester lubricants, on the other hand, are prepared from man-made base stocks having uniform molecular structures giving well-defined properties which can be tailored to specific applications.

Many lubricant requirements are translated into specific properties of an oil measurable by conventional laboratory tests, e.g. viscosity, evaporation, flash point, etc. Other, more critical requirements are related to the chemical properties of the lubricant and many of these can be measured satisfactorily only by elaborate and expensive apparatus specially developed to simulate performance. A wide variety of raw materials can be used for the preparation of ester-type base fluids and this affects a number of lubricant properties including the following:

- viscosity,
- flow properties,
- lubricity,
- thermal stability,
- hydrolytic stability,
- solvency,
- biodegradability.

Viscosity: The viscosity of an ester lubricant can be altered by:

- increasing the molecular weight of the molecule by:
  - increasing the carbon chain length of the acid,
  - increasing the carbon chain length of the alcohol,
  - increasing the number of ester groups.
- increasing the size or degree of branching,
- including cyclic groups in the molecular backbone,
- maximising dipolar interactions.

One disadvantage of very long-chain molecules is their tendency to shear into smaller fragments under stress.

Flow properties: The viscosity index (VI) of an ester lubricant can be increased by:

- increasing the acid chain length,
- increasing the alcohol chain length,
- increasing the linearity of the molecule,
- not using cyclic groups in the backbone, which lowers the VI even more than aliphatic branches,
- by molecular configuration – viscosity indices of polyol esters tend to be lower than their diester analogues, from more compact configurations of the polyol molecules.

The pour point of an ester lubricant can be decreased by:

- increasing branching,
- positioning of the branch – branching in the centre of the molecule gives better pour points than branches near to the chain ends,
- decreasing the acid chain length,
- decreasing the internal symmetry of the molecule.

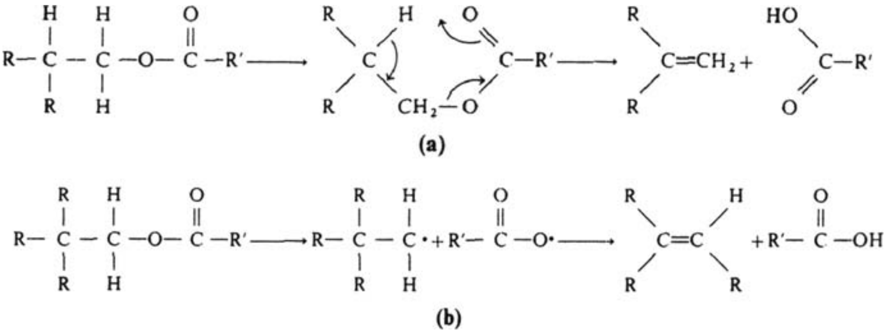
From the above lists, there is a natural trade-off between viscosity index and pour point, e.g. by increasing the linearity of the ester, the viscosity index improves but the pour point increases. Esters made from mixtures of normal and branched acids with the same carbon number have viscosity indices between those of the normal and branched acid esters. But their pour points are lower than those esters formed separately from either branched or normal acids.

Lubricity: Ester groups are polar and therefore affect the efficiency of anti-wear additives. When a base fluid is used which is too polar, it and not the anti-wear additives will be adsorbed onto, and cover, the metal surfaces, giving higher wear characteristics. Consequently, although esters have superior lubricity properties compared to mineral oil, they are less efficient than anti-wear additives. Esters are classified in terms of polarity or non-polarity by the van der Waal formula [48], Equation (2.1):

$$\text{Non-polarity index} = \frac{[\text{Total number of C atoms} \times \text{Molecular weight}]}{[\text{Number of carboxylic groups} \times 100]} \qquad \text{(Eqn. 2.1)}$$

Generally, the higher the non-polarity index, the lower the affinity for the metal surface. Using the above formula it can be seen that as a general rule, increasing molecular weight improves overall lubricity. Esters terminated by normal acids or alcohols have better lubricities than those made from branched acids/alcohols, while esters made from mixed acids/alcohols have lubricities intermediate between esters of normal acids/alcohols and esters of branched acids/alcohols.

Thermal stability: The ester linkage is exceptionally stable; bond energy determinations predict that it is more thermally stable than the C−C bond. The thermal stability advantages of polyol esters compared to diesters is well documented and has been investigated on a number of occasions. The absence of hydrogen atoms on the β-carbon atom of the alcohol portion of an ester leads to superior thermal stability. The presence of the β-hydrogen atom enables a low-energy decomposition mechanism to operate via a six-membered cyclic intermediate producing acids and 1-alkenes, Reaction sequence (2.10a). When β-hydrogen atoms are replaced by alkyl groups, this mechanism cannot operate and decomposition occurs by a free radical mechanism. This type of decomposition requires more energy and can occur only at higher temperatures, as in Reaction sequence (2.10b).



Reaction sequence 2.10 Thermal decomposition of **(a)** esters with β-hydrogens (e.g. dibasic acid esters) and **(b)** esters without β-hydrogens (e.g. neopolyol esters).

Primarily, the oxidative and thermal stabilities of polyol esters are dependent on:

- the absence of hydrogens on β-carbons, as stated above,
- the number and type of hydrogens present in decreasing order of stability,

$$-\mathrm{CH_2}- > -\mathrm{CH}- > -\overset{|}{\underset{|}{\mathrm{C}}}-$$

Thus, in general, linear acid esters are more stable than branched, and short-chain acids are more stable than long-chain acids,

- the stability of the alcohol used, which follow the trend in decreasing order of stability, PE > diPE > TMP > NPG.

One exception to the rule that branched acid esters give poorer stability than linear acids is the branched C_9 acid 3,5,5-trimethylhexanoic acid. The weak tertiary hydrogen is sterically hindered and is more stable than would normally be expected. The structure has fewer secondary hydrogens than the linear form and is hence more stable [49]. Esters made from normal acids generally have higher flash points than those made from branched acids. Increasing molecular weight increases flash points.

Hydrolytic stability: The hydrolytic stability of esters depends on two main features:

- processing parameters,
- molecular geometry.

If the final processing parameters of esters are not tightly controlled, they can have a major effect on the hydrolytic stability of the esters, such as the following:

- their acid value – which must be <0.05 mg KOH/g,
- the degree of esterification, >98%,
- the catalyst used during esterification and the level remaining in the ester after processing, as a low ash level,

before molecular geometry effects will assert themselves. Molecular geometry affects hydrolytic stability in several ways. By sterically hindering the acid portion of the molecule, because hindrance on the alcohol portion has relatively little effect, hydrolysis can be slowed down. For this purpose, geminal di-branched acids such as neoheptanoic acids have been used. However, with these feedstocks there are penalties, namely very long reaction times to achieve complete esterification and also poor pour points. The length of the acid chain is also very important, for acids shorter than pentanoic tend not to be used owing to their corrosivity. The hydrolytic stability of neopolyol esters can generally be regarded as superior to that of dibasic esters.

Solvency: This can be divided into compatibility with additives and other lubricants, and also elastomer compatibility.

> *Compatibility with additives and other lubricants:* Esters are generally fully compatible with mineral oils, which gives them three major advantages. First, there are no contamination problems and therefore esters can be used in machinery that previously used mineral oil. In addition, they can be blended with mineral oil (semi-synthetics) to boost their performance. Second, most additive technology is based on mineral oil experience and this technology is usually directly applicable to esters. Third, esters can be blended with other synthetics such as polyalphaolefins, PAOs, giving them great flexibility, whilst blending with other oils gives unrivalled opportunities to balance the cost of a lubricant blend against its performance.
>
> *Elastomer compatibility:* Elastomers contacting liquid lubricants undergo an interaction with liquid diffusing through the polymer network. There are two possible kinds of interaction, chemical (rare) and physical. During physical interactions two different, and opposing, processes occur:
>
> - extraction of soluble components out of the elastomer, causing shrinkage,
> - absorption of the lubricant by the elastomer, causing swelling. The degree of swelling of elastomeric materials depends on:

- the size of the lubricant – the larger the lubricant, the smaller the degree of swelling,
- the molecular dynamics of the lubricant – linear lubricants diffuse into elastomers quicker than branched or cyclic lubricants,
- the closeness of the solubility parameters of the lubricant and the elastomer – the 'like-dissolves-like' rule is followed,
- the polarity of the lubricant – it is known that some elastomers are sensitive to polar ester lubricants. The non-polarity index can be used to model elastomeric seal swelling trends for specific ester types.

Several polar esters are well-known industrial plasticisers. Non-polar base stocks, such as PAOs, have a tendency to shrink and harden elastomers. By carefully balancing these compounds with esters, lubricants with neutral physical behaviour towards elastomeric materials can be formulated.

Environmental aspects: Increasing environmental awareness has raised water pollution to a major issue. The environment can become polluted in many ways, for example, oils and oil-containing effluents in water can have devastating consequences on fish stocks and other water fauna.

Ecotoxicity: Germany classifies materials according to their potential to pollute water, or 'Wassergefährdungsklasse' (WGK) with substances given a ranking of between 0 and 3, where:

WGK 0	Not water endangering
WGK 1	Slightly water endangering
WGK 2	Water endangering
WGK 3	Highly water endangering

with esters generally having the rankings given below showing that esters have a low environmental impact.

Polyols, polyoleates, C_{36} dimer esters, diesters	WGK 0
Phthalates and trimellitates	WGK 0–2

Biodegradability: The general biochemistry of microbial attack on esters is well known and has been thoroughly reviewed. The main steps of ester hydrolysis [50], β-oxidation of long-chain hydrocarbons [51] and oxygenase attack on aromatic nuclei [52] have been extensively investigated. The main structural features which slow or reduce microbial breakdown are the following:

- the position and degree of branching, which reduces β-oxidation,
- the degree to which ester hydrolysis is inhibited,
- the degree of saturation in the molecule,
- increased molecular weight of the ester.

Figure 2.4 shows the biodegradabilities of a wide range of lubricants as measured using the CEC-L-33-A-94 test [53].

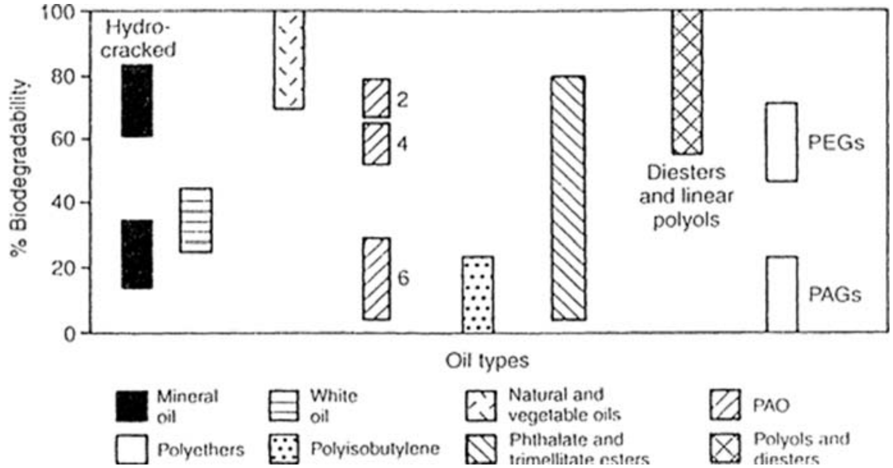


Fig. 2.4 Biodegradability of various lubricants, measured by CEC-L-33-A-94 test [53]

2.6.5 Application Areas

Engine Oils: It is now widely accepted that synthesised fluids, such as polyalphaolefin/ester blends, have inherent performance advantages over conventional petroleum-based oils for the formulation of modern automotive engine lubricants. Practical benefits deriving from their use include improved cold starting, better fuel and oil economy together with improved engine cleanliness, wear protection and viscosity retention during service. Fluid types used in the development of automotive crankcase oils, either commercialised or considered for commercialisation, include polyalphaolefins (PAOs) – more correctly hydrogenated olefin oligomers – organic dibasic esters, polyol esters, alkylated aromatic hydrocarbons and polyglycols. Experience of numerous laboratories from engine bench and vehicle test programmes conducted over the last 20 years shows that blends of PAO and organic esters give an excellent base fluid for the formulation of synthesised crankcase oils [54, 55].

Low-temperature viscosity is arguably the single most important technical feature of a modern crankcase lubricant, for cold starts are a prime cause of engine wear which can be countered only by immediate and effective circulation of the lubricant. Moreover, vehicles are increasingly required to operate reliably under arctic conditions. Esters give the essential low-temperature fluidity and their low volatility does not sacrifice lubricant efficiency at high operating or ambient temperatures. Their low volatility is especially important because of the trend towards smaller sump capacities and longer oil change service intervals.

Two-stroke oils: Esters such as C_{36} dimer esters and polyoleates have several advantages over mineral oils as the lubricant component of two-stroke engine fuel mixtures. First, their clean-burn characteristics result in less engine fouling with considerably reduced ring sticking and lower levels of particulate deposit build-up on ring grooves, skirts and piston undercrowns. Ignition performance and plug life are also enhanced. Second, due to their polar nature, esters are more efficient lubricants than mineral oils – whereas mineral oil has fuel–oil dilution ratios of 50:1, esters can be used at 100:1 and even 150:1. The higher dilution factors give reduced oil emissions which are beneficial for environmentally sensitive applications such as marine outboard engines and chainsaw motors. Third, in some applications, low-temperature performance is important, such as snowmobile-type vehicle engines. Esters with low pour points, down to –56°C, are very suitable for these applications.

Finally, PAHs (polyaromatic hydrocarbons) in exhaust emissions of a two-stroke engine are reduced by 25% when a carboxylic ester is used instead of a mineral oil [56]. PAHs are a major contributor to the carcinogenic nature of exhaust emissions. Esters can also be used to reduce the level of smoke emitted by the engine.

Compressor oils: This market sector covers a wide range of compressor types used for a number of different gases. Diesters and phthalates have found their major application in air compressor lubricants and are also used in natural gas compressors. In reciprocating compressors, where oils of rather higher viscosity are preferred, trimellitate esters can be used. Diesters and polyol esters may also be blended with PAOs for use in various compressor types.

Diesters have inherently good oxidation resistance and low volatilities at 3–10%, according to viscosity, when compared to mineral oil. Together with their higher flash and auto-ignition temperatures and also low orders of toxicity for vapour inhalation, ingestion and skin irritation, these properties make diesters considerably safer lubricants to use than mineral oil. Their low ecotoxicity and high biodegradabilities also lessen their environmental impact. Diesters generally have high viscosity indices, giving a wide temperature range without needing to use viscosity improvers, which can shear in this application. Esters have a further advantage of their good thermal conductivity which conducts heat away from heat sources more effectively than mineral oils. Specific heat values for esters are 5–10% higher than mineral oils, which enables esters to ‘soak up’ more heat and allows compressors to operate at lower temperatures [57].

With chlorofluorocarbons, CFCs, now phased out of use due to their ozone-depleting effects, traditional naphthenic and paraffinic mineral oils used in refrigeration lubricants are being replaced by polyol ester oils. The main reason for the replacement is that traditional mineral oils are immiscible with the more polar hydrofluorocarbons, HFCs, which have replaced CFCs [58].

Aviation oils: The bulk of aviation lubricant demand is for both military and civilian gas turbine lubricants. Hydrocarbon oils cannot meet the requirements placed on jet engine oils, primarily lubrication, oxidation and ageing stability. Type 1, the first generation of oils were diesters but over the last 30 years have lost ground to the more expensive polyol esters, Type 2. Some diesters are still used in less demanding applications such as for small private aircraft and turbo-prop engines. Type 2 aviation gas turbine lubricants are produced to a viscosity of 5 cSt at 100°C but for some military applications where low-temperature operability is vital, this is reduced to 3 cSt.

2.6.6 Future Trends

The requirement for lubricants to operate at higher temperature has caused a move away from mineral oil base oils to esters. Due to the better temperature stability of polyols, there is a growing tendency to use them in preference to diesters. Responding to increased environmental quality requirements, ester chemistry has been modified to produce compounds with high biodegradability, low toxicity and very low engine emissions.

2.7 Polyalkylene Glycols

2.7.1 Introduction

The term ‘polyalkylene glycol’ applies to an extensive range of polymeric molecules which, depending on their chemical structure, can have quite different physical properties. For example, polyalkylene glycols can be solid or liquid, water soluble or water insoluble, and can be produced to almost any required viscosity. Polyalkylene glycols have the following inherent chemical and physical properties which make them suitable for a large number of engineering and lubrication applications:

- wide viscosity range,
- excellent viscosity/temperature characteristics,
- low pour points,
- good thermal stability,
- high flash points,
- good lubricity,
- low toxicity,
- good shear stability,
- water solubility or insolubility,
- non-corrosive to common metals,
- volatile or soluble breakdown products,
- little effect on rubbers,
- practically non-flammable in aqueous solution.

Typical application areas are industrial gear oils and greases, compressor lubricants, metalworking fluids, aqueous quenching fluids, fire-resistant hydraulic fluids, textile lubricants and heat transfer liquids. Section 2.7.5 gives a detailed account of these applications.

2.7.2 Production

Polyalkylene glycols are produced by reacting compounds containing active hydrogen atoms, e.g. alcohols, water, with alkylene oxides (also referred to as oxiranes or epoxides), usually in the presence of a basic catalyst such as sodium or potassium hydroxides or tertiary amines. The commonly used alkylene oxides are ethylene oxide and propylene oxide, Fig. 2.5. Alkylene oxides are very reactive and readily polymerised in highly exothermic reactions. Under basic polymerisation conditions, ethylene oxide gives products with exclusively primary terminal hydroxyl groups, whereas propylene oxide preferentially gives secondary terminal hydroxyl groups, Reaction sequence (2.11), which shows a typical polymerisation reaction for an alcohol, ROH, with KOH as catalyst. Although only a small number of alkoxide ions, i.e. RO^-, are present in the reaction mixture at any time, for only a catalytic quantity of KOH is added, continuous fast exchange of protons results in products of relatively narrow molecular weight distributions. Products are normally characterised by an average molecular weight or by their viscosity. When polymerisation is complete, the residual catalyst can be (i) neutralised, e.g. by the addition of phosphoric acid; (ii) demineralised, e.g. by using amphoteric aluminosilicates; or (iii) left in the product.

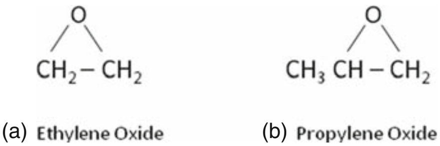
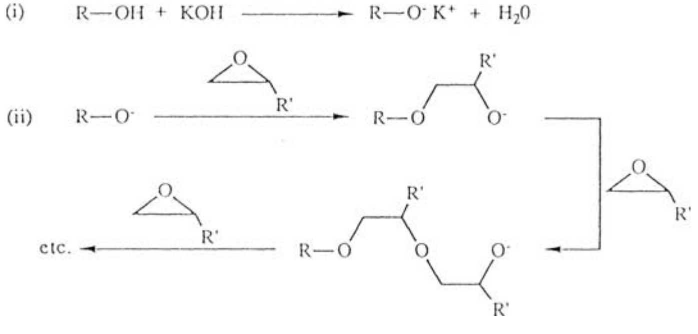


Fig. 2.5 Structures of **(a)** ethylene oxide and **(b)** propylene oxide



Reaction sequence 2.11 Typical polymerisation reaction for an alcohol with KOH as catalyst

2.7.3 Chemistry

The ether linkages in polyalkylene glycols are responsible for the unique properties of these polymers. The carbon–oxygen bond of an ether is stronger at 351 kJ mol^{-1} than the carbon–carbon bond of a hydrocarbon at 348 kJ mol^{-1} and the electron-rich oxygen atoms offer many sites for co-ordination. Hydrogen bonding to these sites gives water solubility to many of these molecules. The polarity resulting from the oxygen atoms also confers quite different gas solubilities. Obvious routes to controlling product properties are the following:

- variation of the starting molecule (initiator),
- variation of the alkylene oxide(s) used,
- the molecular weight.

Initiators: Typical initiators include butanol (monofunctional), ethylene or propylene glycol (difunctional) and trimethylol propane (trifunctional). Both mono- and difunctional initiators give products with linear chains but the monofunctional-based products have half of the chain ends capped by an alkyl group. Tri- and polyfunctional initiators give products with branched chains.

Alkylene oxide(s): The vast majority of commercialised polyalkylene glycols are based on ethylene oxide only, propylene oxide only or copolymers incorporating the two. Copolymers can be synthesised as ‘random’ (oxides added as a mixture giving a statistical distribution throughout the chain) or ‘block’ (oxides added separately). Due to the more reactive nature of ethylene oxide, random copolymers will tend to preferentially incorporate propylene oxide units at the chain extremities.

Polyalkylene glycols for use in engineering and lubrication applications are usually homopolymers of propylene oxide or random copolymers. The relative proportions of ethylene oxide and propylene oxide have significant effects on several properties, e.g. pour point, water solubility and pressure–viscosity relationship.

Molecular weight: By controlling the quantity of oxide added, polyalkylene glycols with a wide range of molecular weights (and hence viscosities) can be selected. The ability to ‘engineer’ polyalkylene glycol molecules in this way distinguishes them from most other products used in similar applications. Viscosities at 40°C can be achieved from as low as 8 cSt to greater than 100,000 cSt.

2.7.4 Key properties

Water solubility: As previously mentioned, polyalkylene glycols can be either water soluble or water insoluble. Water solubility is primarily governed by the ratio of ethylene oxide:propylene oxide in the polymer, with a higher proportion of ethylene oxide leading to greater solubility. Molecular weight also influences water solubility, although to a much lesser extent, with lower molecular weight polymers showing greater solubility. Homopolymers of propylene oxide are effectively water insoluble, except for very low molecular weight of <900 amu. Typical oxide ratios used for water-soluble copolymers are between 1:1 and 3:1 ethylene oxide:propylene oxide (by weight).

All polyalkylene glycols exhibit inverse solubility in water, i.e. water solubility decreases as temperature increases. This is explained by the loss of hydrogen bonding at elevated temperatures. The temperature of polymer/water separation is usually referred to as the cloud point and is higher for copolymers with larger proportions of ethylene oxide.

Pour point: Polyalkylene glycols with high proportions of propylene oxide, $> 50\%$, exhibit very low pour points, down to –50°C. This results from the lateral methyl groups of the propylene oxide unit disrupting crystallisation. Table 2.9 shows a typical comparison.

Table 2.9 Comparison of pour points for two polyalkylene glycols with different proportions of propylene oxide

Product	Molecular weight (amu)	Ethylene/Propylene oxide ratio	Pour point (°C)
PEG 1000	1000	1:0	+37
VG 70 W	1300	1:1	–46

Viscosity–pressure behaviour: The relationship between viscosity and pressure, the pressure viscosity coefficient, is an important parameter for lubrication performance. Higher values are obtained for polymers with a high degree of propylene oxide units.

Viscosity index: Polyalkylene glycols typically exhibit excellent viscosity/ temperature characteristics. For example, Emkarox VG 222, ISO 220, has a VI of 215, which is significantly better than that for an equivalent ISO grade mineral oil VI of $\sim$100. The viscosity index tends to be better for products with a low degree of chain branching.

Degradation: In contrast to mineral oils, polyalkylene glycols form either volatile or soluble degradation products upon oxidation and do not leave unwanted solid deposits during service. Thermal stability is significantly improved by the addition of antioxidants.

Lubrication: Polyalkylene glycols show very good frictional behaviour and are inherently excellent lubricants. Their highly polar nature gives a strong affinity to metals and thus lubrication films remain adherent even at high surface pressures, giving low abrasive wear.

2.7.5 Applications

Introduction: Polyalkylene glycols (PAGs) were first developed in the mid-19th century but were not used commercially until the late 1930s as a castor oil replacement in automotive brake fluids. The compulsory use of fire-resistant hydraulic fluids, triggered by the death of 250 miners in the Belgian pit disaster of 1956, resulted in a substantial increase in PAG consumption. During the 1960s, PAGs were used in heat treatment foundries to quench metal. A combination of inherent inverse solubility and fire-resistant properties provided an alternative to mineral oil-based products.

Following strong growth during the 1970s and 1980s, PAGs are now used for many applications worldwide and constitute the largest market share within the synthetic lubricant sector. What of the future? – there is a belief that 'current' PAGs may be close to their peak market share but developments of new products with improved application performance may give further growth.

Brake fluids: Two predominant types of brake fluid formulations, DOT 3 and DOT 4, based on specifications issued by the US Department of Transport, are used in Western Europe. Due to increased demands placed on brake fluids, particularly with regard to water absorption, much of the polyglycol has been replaced by borate esters. However, the lubricity, limited rubber swell and low pour points of these esters means that a typical DOT 4 formulation may contain up to 10% PAG.

Fire-resistant fluids: A major application of PAGs involves their use in fire-resistant fluids. Industrial sectors such as steel production, die casting (where leaks in high-pressure hydraulic lines can create serious fire hazards) and mining (where the consequences of fire are catastrophic) have generated a large demand for these types of hydraulic fluids; indeed many countries now legislate their use. Fire-resistant fluids have been classified by several international bodies:

- ISO – International Organisation for Standardisation,
- CETOP – Comité Européen des Transmissions Oleohydrauliques et Pneumatiques,
- Luxembourg Commission – Commission of the European Communities: Safety and Health Commission for the Mining and Extractive Industries.

The following designations are used:

- *HFA* fluids containing more than 80% water, formulated with either mineral oil, synthetic chemical solution or synthetic emulsion,
- *HFB* water-in-oil (invert) emulsion, water content 40–50%,
- *HFC* water-polymer solution, minimum water content 35%,
- *HFD* water-free chemical fluid.

High molecular weight PAGs, 12–30K amu, are found to be particularly suitable for the formulation of the HF-C type of fluid. PAG, water (35% minimum) and glycol, and together with anticorrosion, anti-wear and antifoam additives, are formulated to conform to manufacturers' specifications for particular systems. Stringent flammability requirements, corrosion protection, low levels of wear, foaming and other demands such as viscosity and air release must all be achieved.

Compressor lubricants: Lubrication in the pressurised area of a compressor presents many problems. Lubricants must not only seal, cool and reduce friction and wear but also cope with the presence of compressed aggressive or oxidising gases.

The polarity of PAGs, particularly the water-soluble type, significantly lowers the solubility of hydrocarbon gases such as methane and ethylene compared to the equivalent mineral base oil-derived lubricants. In practice, this means that compressors for hydrocarbon and other chemical gases can be operated without lowering lubricant viscosity, resulting in increased efficiency. For example, in low-density polyethylene compressors operating at 2000–3000 bar, the solubility of ethylene in water-soluble PAG is less than 15% of that observed with white oils. This has the added benefit of reducing lubricant contamination of the final product, an important consideration for food packaging-grade polythene.

Metal cutting: This operation involves the removal of metal as chips from a workpiece component. Two principal types of fluids are used to cool and lubricate:

- neat mineral oil,
- soluble oils.

There is a small demand within the soluble oil sector for fully synthetic 'true solutions', particularly for light-duty and grinding applications. These solutions may be formulated using water-soluble PAGs as base stock where their inverse solubility characteristic is advantageous in coating metal surfaces with a film of polymer to give lubrication and reduced tool wear. Biostability, low toxicity and little or no skin irritancy are additional benefits.

Gear oils and greases: The fundamental purpose of a lubricant is to reduce friction between moving parts, hence lowering temperature and improving efficiency. Increased industrial demand for high-performance lubricants has resulted in a much wider acceptance of synthetic-based products. PAGs are extensively used to lubricate calendar gears and bearings within the plastics, rubber and paper industries, being particularly suited for heavily loaded worm gears. Efficiency of a worm gear is related to the friction between drive and gear wheel and within the contact there is a high degree of sliding which increases operating temperatures. Consequently, a lubricant must not only have a low coefficient of friction but also have a high viscosity index and good thermal and oxidative characteristics.

Paper and concrete mills are examples of processes where ingress of dust and moisture gives particular problems. Gear oils based on water-soluble PAGs can be used for easier cleaning and extended service intervals.

Both water-soluble and water-insoluble types of PAGs can be used in the formulation of synthetic greases. Thickening is achieved either by conventional soap technology or by addition of solids such as modified bentonite clays or fine particle size silica. The clean burn-off characteristic of all PAGs makes them particularly suitable as grease bases incorporating molybdenum disulphide or graphite. The PAGs form volatile oxidation breakdown products, leaving no carbonaceous residues or sludge. A typical application is chain lubrication in very high-temperature ovens.

Textiles: Two important criteria must be considered during fibre processing: (i) drag from hard surfaces causing fibre damage and (ii) excessive lubrication between the individual filaments causing fibre/fibre slippage, thus impairing the process. An ideal spin-finish formulation strikes a balance between fibre/fibre static friction and fibre/hard-surface dynamic friction. PAGs have several advantages over mineral oils and simple esters:

- little or no carbonaceous residue is produced when the lubricant is volatilised during high-temperature texturising and high-speed spinning,
- viscosity and cloud points (inverse solubility) can be readily varied according to requirements,
- scourability is good, important when polishing the fibres,
- water solubility at ambient temperatures assists application, film coverage and removal.

A typical spin-finish concentrate would consist of lubricant (usually blended), 75–85%, antistat, 5–10%, and additives (antioxidants), 5–10%. Formulations of textile machine lubricants based on water-soluble PAGs combine gear lubricity with ease of removal from fibres during processing.

Rubber lubrication: The negligible swelling characteristics of water-soluble and water-insoluble PAGs are used to advantage within the rubber industry. Applications include antistick agents for uncured rubber, demoulding fluid in tyre production, mandrel lubricants for hoses, and lubricants for rubber packings, ‘O’ rings and seals. PAGs can be formulated with solvents and wetting agents, and applied directly by brush or spray.

Two-stroke engine lubrication: Synthetic lubricants virtually eliminate engine problems associated with deposition and fouling, commonly seen with mineral oil lubricants. Although esters are predominant in this application, PAGs tend to have special uses, for example, with model engines where a mixture of PAG/methanol provides a cleaner alternative to castor oil-based fuels.

2.8 Phosphate Esters

2.8.1 Introduction

Phosphate esters have been produced commercially since the 1920s and now have important applications as plasticisers, lubricant additives and synthetic-based fluids for hydraulic and compressor oils. Their first use in lubrication was as anti-wear additives. Later developments in aircraft hydraulic control systems, particularly during the Second World War, introduced phosphate esters as less flammable hydraulic fluids. As esters of orthophosphoric acid they have the general formula $OP(OR)_3$, where R represents an aryl or an alkyl group or, very often, a mixture of alkyl and/or aryl components. The physical and chemical properties of phosphate esters can be varied considerably depending on the choice of substituents [59, 60], selected to give optimum performance for a given application. Phosphate esters are particularly used in applications that benefit from their excellent fire-resistant properties, but compared to other base fluids they are fairly expensive.

2.8.2 Manufacture

Phosphate esters are produced by reaction of phosphoryl chloride with phenols or alcohols, or, less commonly, sodium phenoxides/alkoxides, as Reaction (2.12):

$$3ROH + POCl_3 \longrightarrow OP(OR)_3 + HCl \qquad \text{(Reaction 2.12)}$$

Early production of phosphate esters was based on the ‘crude cresylic acid’ fraction or ‘tar acids’ from coal tar residue distillation. This feedstock is a complex mixture of cresols, xylenols and other materials. It includes significant quantities of *ortho*-cresol, resulting in an ester with marked neurotoxic effects. This has led to the use of controlled coal tar fractions, where the *ortho*-cresol and other *ortho*-*n*-alkylphenol content is greatly reduced. Phosphate esters using coal tar fractions are generally known as ‘natural’, as opposed to ‘synthetic’ where high-purity materials are used.

The vast majority of modern phosphate esters are ‘synthetic’, using materials derived from petrochemical sources. For example, alcohols are from α-olefins by the OXO process and iso-propylated or *t*-butylated phenols are produced from phenols by reaction with propylene or butylene. Reaction of alcohol or phenol with phosphoryl chloride yields the crude product, which is washed, distilled, dried and decolourised to yield the finished product. Low molecular weight trialkyl esters are water soluble and require non-aqueous techniques. For mixed alkylaryl ester production the reactant phenol and alcohol are added separately, the reaction being conducted in a stepwise fashion. Reaction temperatures are kept as low as possible to avoid transesterification reactions.

2.8.3 Physical and Chemical Properties

The physical properties of phosphate esters vary considerably according to the mix and type of organic substituents, the molecular weights and structural symmetry proving particularly significant [59]. Consequently, phosphate esters range from low-viscosity, water-soluble liquids through to insoluble, high-melting solids.

The use of phosphate esters arises mostly from their excellent fire resistance and superior lubricity but is limited by their hydrolytic and thermal stability, low-temperature properties and viscosity index.

The hydrolytic stability of aryl esters is superior to the alkyl esters but increasing chain length and degree of branching of the alkyl group leads to considerable improvement in hydrolytic stabilities. However, the more sterically hindered the substituent, the more difficult to prepare the ester. Increased chain branching leads to a progressive drop in viscosity index. Alkyl–aryl phosphates tend to be more susceptible to hydrolysis than are the triaryl or trialkyl esters. Hydrolysis has potentially serious consequences as it produces acid esters which can lead to corrosion and may also catalyse further degradation.

The thermal stability of triaryl phosphates is considerably superior to that of the trialkyl esters, which degrade thermally by a mechanism analogous to that of the carboxylic esters, Reaction (2.13):

(Reaction 2.13)

The use of neopentyl alcohol or its homologues yields a β-hindered ester which blocks this decomposition mechanism, giving much improved thermal stability. However, esterification is problematic and expensive, and the esters have mediocre

VIs and consequently β-hindered esters are not generally used in lubrication. Triaryl phosphates have better oxidative stability than that of the trialkyl esters, with triphenyl phosphate showing no degradation up to 340°C. Phosphate esters are generally stable to oxidation up to, and above, the point of significant evaporation.

Low-temperature properties of phosphate esters containing one or more alkyl substituents tend to be fairly good, with pour points of –55°C being common. Many triaryl phosphates have fairly high melting points but an acceptable pour point can be achieved by using a mixture of aryl components. The use of coal tar fractions to make 'natural' phosphate esters are already complex mixtures and give esters with satisfactory pour points.

The effects of molecular mass and shape on viscosity and VI are similar to that of other base fluid types. Increasing the length of straight-chain alkyl substituents increases viscosity and VI but has a negative effect on low-temperature performance with increased pour points. Increased branching of alkyl substituents, for constant molecular weight, gives lower viscosities and VIs but improved pour point.

Phosphate esters are very good solvents and extremely aggressive towards paints and a wide range of plastics and rubbers. Therefore, careful consideration is required when selecting suitable gasket and seal materials for use with these esters. As an example, ethylene–propylene rubbers and poly-urethane or epoxy-cured paints may generally be used. The solvency power of phosphate esters is advantageous in making them compatible with most common additives and enables them to be used as blends with other base fluid types for a number of applications. Indeed, the presence of phosphate esters in a formulation may help to solubilise other additives.

As mentioned previously, the most important properties of phosphate esters are their fire resistance and lubricity. They have high, though not exceptional, flash points and generate phosphoric acid on pyrolysis, a powerful flame retardant, giving their excellent flame-retardant properties. They have extremely good lubricity, as demonstrated by their wide use as load-carrying additives in a range of lubricants. When used as an additive or a base fluid, phosphate esters give boundary lubrication by chemically binding with metal surfaces as thin layers of iron phosphates and/or phosphides. The applied friction force shears these surface films in a sacrificial manner to protect the metal surface below. As base fluids they have exceptional load-carrying and anti-wear properties, well in excess of other unformulated synthetic base fluids.

2.8.4 Applications

Hydraulic fluids used close to a potential source of ignition such as a hot surface are a serious fire hazard. In such circumstances, phosphate esters are used particularly for their inherent fire resistance and where their moderate cost can be borne. Fire-resistant hydraulic fluids are the largest volume use of phosphate esters; in addition they give lubrication equal to that of formulated hydrocarbon fluids. Other requirements such as viscosity or thermal stability can be met by appropriate choice of substituents. Industrial fire-resistant fluids are often required to operate at sustained high temperature and only the triarylphosphate esters can give satisfactory thermal stability. These fluids are used in foundries, die casting, aluminium smelters, mines and in applications such as injection moulding, oven door controls and automatic welding equipment.

Phosphate esters are also used as hydraulic fluids in civil aircraft where thermal stability is less important than their low-temperature viscosities and cold flow properties. Trialkyl and alkyl–aryl phosphates are used which, when formulated with a VI improver, give fluids with pour points of –55 to –65°C and a VI of 170–300. They are also chosen for other low-temperature applications for conditions such as those found on North Sea, and similar weather condition, oil rigs.

2.9 Synthetic Base Oil Categorisation

To recall and extend Section 1.8 from the previous chapter, the quality of lubricant base oils is categorised by the American Petroleum Institute and used in lubricant specifications worldwide, described in API 1509 (API 2007). Groups I–III were described previously and are reproduced here for comparison:

- Group I base stocks contain <90% saturates and/or >0.03% sulphur with a viscosity index $\geq$80 and <120,
- Group II base stocks contain $\geq$90% saturates and $\leq$0.03% sulphur with a viscosity index $\geq$80 and <120,
- Group III base stocks contain $\geq$90% and $\leq$0.03% sulphur with a viscosity index $\geq$120,
- Group IV base stocks are polyalphaolefins (PAOs),
- Group V base stocks include all other base stocks not included in the previous Groups I–IV, thus the polybutenes, synthetic esters, polyalkylene glycols and the phosphate esters are all included in this group.

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Part II
Additives

Chapter 3
Friction, Wear and the Role of Additives in Controlling Them

C.H. Bovington

> *All things and everything whatsoever, however thin it be, which is interposed in the middle between objects that rub together, lighten the difficulty of this friction*
>
> Leonardo Da Vinci 1452–1511 [1]

Abstract The laws of friction are described. Abrasive, adhesive, contact fatigue and corrosive wear mechanisms are explained. The tribological regime of boundary lubrication is discussed in the context of the Stribeck curve and surface film formation. Physical processes for surface film formation and their properties are examined for oxygen-, nitrogen-, sulphur-, phosphorus, boron, molybdenum-containing organic compounds and ZDDP in particular. ZDDP film formation is discussed in depth and the influence of dispersants described. Interactions between reduced ZDDP levels and molybdenum compounds to maintain wear protection and antioxidancy are considered for the requirements of lower SAPS formulations in future formulations.

3.1 Introduction to the Mechanisms of Friction

Friction is the resistance to motion of one body in contact with another and is proportional to the applied load but independent of the sliding surface area. These laws are attributable to Leonardo Da Vinci [1], then rediscovered by Amontons in 1699 [2]. In 1781 Coulomb distinguished between static friction, the force required to start sliding, and kinetic friction, the force required to maintain motion [3]. He showed that kinetic friction is lower than static friction and is nearly always independent of the speed of sliding. To understand the causes of friction, the following must be considered:

(i) Even the most carefully prepared surfaces contain peaks (called asperities) and valleys which are large compared with molecular dimensions. The solid surfaces contain peaks of these highest asperities, so the area of intimate contact reach between them is very small. The real area of contact is influenced

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by the magnitude of the applied load since under the intense pressure of the localised points of contact, plastic deformation and flow occurs until the area is sufficiently great to support the load.

(ii) When sliding takes place, all of the friction occur over the very small contact area and surface temperatures at the rubbing asperity contacts reach very high values. This heating effect may cause micro-structural changes to asperities as well as local melting.

(iii) At the points of asperity contact, there are real adhesions and welding together of the two surfaces. The frictional force is mainly the force required to shear these junctions.

The classic laws of friction can now be understood since the contact area over which the junctions are formed is almost independent of the apparent, dimensional, area of the sliding surface and is directly proportional to the applied load. With static surfaces, or at low sliding speeds, cold welding is produced by the intense pressure in the region of contact. At higher speeds it is assisted by the high-temperature softening or melting of the metal surface.

The energy required to shear these asperity welds accounts, in part, for metal to metal friction; there is a further component contributing to the overall friction, 'ploughing'. This is the force F_{p} required to displace the softer metal of the two dissimilar metals in sliding contact. The total frictional force F_1 is given by Equation (3.1) as:

$$F_1 = F_{\mathrm{A}} + F_{\mathrm{p}} \qquad \text{(Eqn. 3.1)}$$

where F_{A} is the force needed to shear adhesive junctions, $= A_{\mathrm{c}}S$, A_{c} is the real area of contact, taking account of the elasticity of the two surfaces, S is the effective shear stress of the junctions.

For most combinations of materials, F_{p} is the minor contribution so that μ, the coefficient of friction, is given by Equation (3.2) as:

$$\mu = F_1/W = F_{\mathrm{A}}/W = S/H \qquad \text{(Eqn. 3.2)}$$

where H is the effective surface hardness, W is the applied load and S is the shear strength. From these simple theories, it follows that for low friction the sliding materials must have the following:

- low shear strength,
- high hardness.

These requirements are met if *thin* low-shear-strength layers are formed on hard metal substances. The low-shear-strength layer must be thin enough not to yield significantly and thus increase the real area of contact A_{c}. Later sections of this chapter examine how lubricant additives can provide a low-shear-strength film and can, in many cases, militate against the ploughing effect in those cases where ploughing is a significant contribution to overall friction.

3.2 Mechanisms of Wear

Wear is the process of physical loss of material. In sliding contacts this can arise from a number of processes; in order of relative importance they are adhesion, abrasion, corrosion and contact fatigue. Wear occurs because of local mechanical failure of highly stressed interfacial zones and the mode of failure is influenced by environmental factors.

3.2.1 Adhesive Wear

Bonding, or cold weld formation, can occur at the asperity tips of contacting, loaded, surfaces. This is the first stage of a wear mechanism and does not lead directly to any loss of material from the system. The bonded section may be work hardened, and hence strengthened, and shear may occur not at the asperity tip junctions but within the body of the material. This transfers material from one surface to the other and no overall wear occurs until a secondary process causes the transferred material to break away. Sometimes transferred material resides in a surface and may even transfer back to the original surface. However, groups of particles can be formed which break away as a single entity when the elastic energy just exceeds the surface energy, the latter being greatly reduced by environmental reaction.

Adhesive wear processes can be viewed as a state of dynamic equilibrium with their environment. The fresh surfaces exposed by wear are more reactive than the original surface and must be passivated by additives if wear is not to be catastrophic. Many wear processes commence as adhesive wear but the fact that this mechanism leads to the formation of abrasive debris inevitably means that there is a possible transition of the wear mechanism from adhesive to abrasive. Adhesion and adhesive wear can be limited by:

- using metal combinations which do not bond together easily,
- improving the formation of low-shear-strength additive layers,
- increasing the oil film thickness.

3.2.2 Abrasive Wear

Wear caused by the presence of hard particles in the contact is very similar to grinding or machining operations, although with less efficiency. During abrasion a metal undergoes extensive work hardening. For this reason the initial hardness of the abrasive particle is unimportant if the heat-transformed wear particle is substantially harder than that of the metal surfaces. Should the wear particle present in the contact become softer due to thermal processes generated by friction, then the particle will be deformed under the contact pressure and damage to the sliding surfaces is minimised. Examples of frictional hardening and softening are well documented and can be predicted from the phase diagrams of metals.

The majority of engineering materials are heterogeneous, composed of phases with considerable differences in hardness. When an abrasive particle is small, the presence of coarse, hard, phases in these alloys can considerably strengthen the material's resistance to abrasive wear. But if the abrasive particle size is comparable to the scale of heterogeneity of the material, then gouging out the hard material from the structure leads to an increased wear rate. Abrasion can be limited by:

- increasing the hardness of the rubbing surfaces,
- putting soft coatings onto surfaces to embed debris, e.g. soft crankshaft-bearing materials,
- improving oil filtration,
- increasing oil film thickness,
- reducing surface roughness.

3.2.3 Contact Fatigue

Although fatigue mechanisms can operate under sliding conditions, they tend to predominate in rolling contacts where stresses are high and slip is small. This wear fatigue mechanism causes pitting or spalling of the surfaces.

This type of surface failure manifests itself by the breakout of small, roughly triangular portions of the surface material. It occurs primarily due to high stresses which cause fatigue failure to commence at a point below the surface where the highest combined stresses occur. After initiation, encouraged by impurity inclusions, tangential traction and the hydraulic forces generated by lubricants, propagation occurs parallel to the surface until a structural weakness such as a grain boundary is encountered. The crack then propagates to the surface. Hydraulic action of the lubricant under contact pressures can help to lever out the triangular pits. Surface treatments and material property change in service can influence the fatigue life of the contacting materials.

Although the maximum cyclic stress occurs a few micrometres below the immediate surface, the presence of surface flaws means that surface crack propagation will become competitive with those of sub-surface origin. Fatigue damage can be limited by:

(i) increasing the lubricant film thickness,
(ii) minimising the influence of entrained or dissolved water,
(iii) reducing sliding, relative to rolling motion, in the contact,
(iv) addition of fatigue-limiting additives.

3.2.4 Corrosive Wear

This type of wear loses material by chemical reaction and can be very detrimental to service life, e.g. the acidic corrosion of cylinder liner materials. If it is controlled, however, it can be beneficial such as the formation of low-shear-strength boundary lubricant films by extreme pressure (EP) or anti-wear (AW) additives. A lubricated system contains many corrosive species, such as:

(i) oxygen,
(ii) water,
(iii) carbon dioxide,
(iv) naturally occurring sulphur compounds,
(v) acidic combustion products, oxyacids of nitrogen or sulphur,
(vi) acidic oil oxidation products,
(vii) anti-wear and extreme pressure additives.

All of these have a tendency to chemically attack metals and rubbing usually enhances such attack by:

(i) removal of surface corrosion product layers, exposing fresh metal to attack,
(ii) raising surface temperatures to speed diffusion and increase reaction rates.

Corrosion can take place uniformly over a rubbed surface or selectively at surface inclusions, grain boundaries and between dissimilar materials, etc. For the former case, a problem results only if corrosion is excessive. Limited corrosion is necessary for anti-wear and extreme pressure protection. Selective corrosion can weaken surface structures and initiate fatigue. Moreover, abrasion is implicated in the promotion of corrosive wear since abrasive particles remove soft protective, corrosively formed, reaction films.

For engines using modern diesel fuels, with relatively low levels of sulphur, corrosive cylinder linear wear is not a problem, provided that adequate overbased detergents are present in the lubricant to neutralise the sulphur acids produced by combustion. The rate of formation of reacted films usually follows the Arrhenius Law, as in Equation (3.3):

$$\text{Reaction rate} = KC\mathrm{e}^{-E/RT} \qquad \text{(Eqn. 3.3)}$$

where C is the reactive component concentration in the oil, E is an energy constant to describe the reactivity of the component, T is the absolute temperature in °K of the surface, R is the universal gas constant and K is the pre-exponential factor.

In the steady state the role of corrosive wear is usually determined by the state of film build-up. Therefore, wear rates increase linearly with concentration and exponentially with temperature. Corrosion can be limited by:

(i) using corrosion and rust inhibitors,
(ii) using additives of the minimum activity needed to prevent adhesion,
(iii) limiting water access and activity,
(iv) neutralisation by overbased detergents.

3.3 Boundary Lubrication

Boundary lubrication describes processes which can occur at surfaces in relative motion to reduce friction and also control wear under conditions where fluid film formation is not possible. Boundary lubrication functions by several mechanisms which often operate simultaneously, all of which counter one or both of the general causes of friction (and hence wear) previously described, i.e. the reduction of energy required to shear asperity junctions and a reduction in ploughing.

3.3.1 Mechanisms of Film Formation

These mechanisms include the following:

(i) *Formation of a layer of molecules adsorbed by van der Waals forces:* To form such layers a molecule must have a polar end which attaches to the metal – attachment through more than one polar group is also possible – and a non-polar end which points out into the oil solution; Fig. 3.1 illustrates such film formation. These layers are a shear strength layer which allows motion without high friction and can also reduce wear. The temperature/load range over which they are effective depends upon their individual structure.

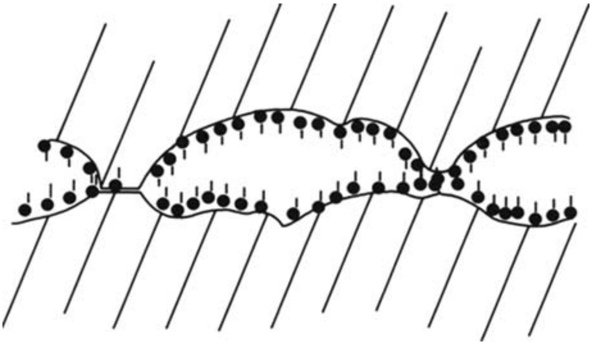


Fig. 3.1 van der Waals adsorption

(ii) *Formation of high-viscosity layers:* Layers formed by the reaction of oil components in the presence of rubbed metal surfaces can produce relatively thick, >10 μm, layers of high-viscosity material which can be globular or continuous, Fig. 3.2. This film gives a hydrodynamic effect even at low speeds and may be linked to the surface by van der Waals forces. These films tend to be less effective under high contact loads.

(iii) *Thin reacted layer plus smoothing:* Oil components chemically attack exposed clean metal surfaces to give a thin, chemically altered layer, e.g. a soap, Fig. 3.3. Chemical film formation does not occur to any appreciable depth and abrasion plus this attack smoothes asperities. This fact, together with the low shear strength of the film, leads to reduction of adhesion and ploughing. Moderate temperatures are often required for the formation of these films.

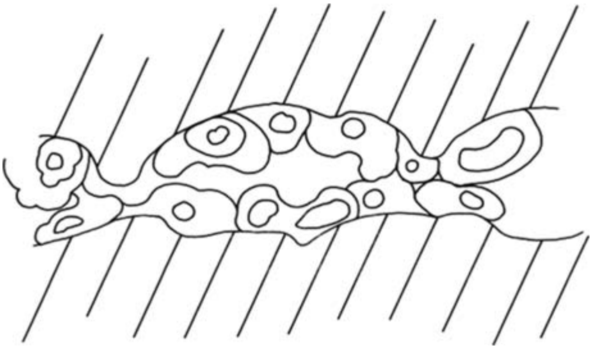


Fig. 3.2 High-viscosity layer formation

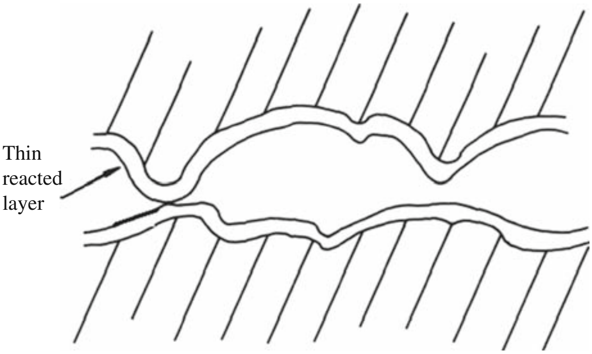


Fig. 3.3 Thin reacted layer and smoothing

(iv) *Thick reacted inorganic layers:* Reaction between active oil components and metal surfaces forms thick, reacted, low-shear-strength inorganic films such as sulphides on the sliding surfaces, Fig. 3.4. This surface layer limits adhesion but must be reformed as quickly as is practicable or scuffing will occur. These films are usually formed only at high temperature and loads.

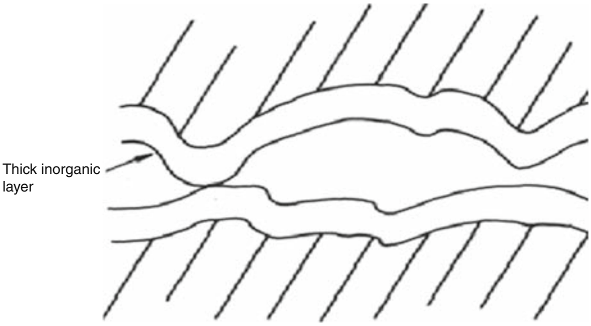


Fig. 3.4 Thick reacted inorganic layer

(v) *Rehbinder effect:* Chemicals can weaken metals by the Rehbinder effect, Fig. 3.5. The precise mechanisms of this effect are unclear but may involve hydrogen embrittlement. The effect is to minimise ploughing and hence control friction and wear. From a practical standpoint, it is the least important of the five mechanisms.

Fig. 3.5 Rehbinder weakening of surface layers

3.3.2 Conclusion

Dependent upon load, speed, viscosity, temperature and the nature of the lubricated surfaces in relative motion, differing degrees of separation of these surfaces occur. When significant oil film penetration occurs, frictional heating begins to cause wear, and then both friction and wear can be controlled by chemical/physical surface reactions. Within an engine a range of the above conditions operate. The influence of these conditions on friction can be seen from the Stribeck curve, Fig. 3.6.

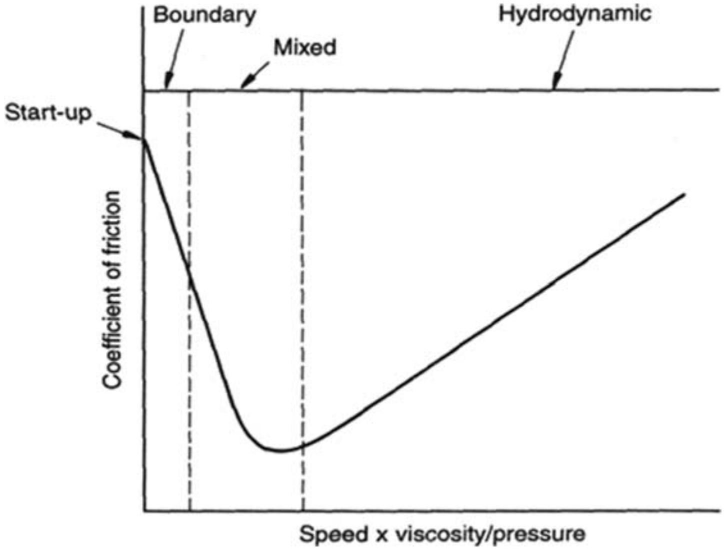


Fig. 3.6 The Stribeck curve

The challenge to the chemist is to minimise this friction whilst controlling wear at the same time. Although both friction and wear are greatly influenced by the shear strength of the junction formed between the contacting asperities, control of friction does not automatically lead to reduced wear.

3.4 Physical Chemical Processes for the Formation of Surface Films

3.4.1 Formation of Surface Films

The process of surface film formation by additives involves a series of steps, described as:

- interactions between permanent dipoles in the molecule and fluctuating dipoles on the surface,
- residence at the surface,
- desorption back into solution or,
- chemical reaction between the adsorbed species and the surface,
- diffusion of species to the surface.

Dependent upon temperature and additive concentrations, any of the above can be the rate-limiting step controlling film formation. The issue is further complicated by the temperature-variable influence of interactions of molecules in solution. These can influence the equilibrium between surface and solution by influencing the flux of molecules/unit time impinging upon the surface and the probability of reaction at the surface. To a reasonable approximation, the kinetics of these processes can be described by the Langmuir isotherm, Equation (3.4):

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = k_{\mathrm{a}}\,[\mathrm{A}]\,(1-\theta) - k_{\mathrm{d}}(\theta) \qquad \text{(Eqn. 3.4)}$$

where θ is the surface coverage, [A] is the concentration of additive in solution, k_{a} and k_{d} are the rate constants for adsorption and desorption, respectively (i.e. all surface sites are equivalent) and t is the time.

Equations of this type can describe both the ‘physical’ dipole/dipole interactions and the subsequent ‘desorption’ from the film. Since k_{a} and k_{d} have different temperature coefficients, increasing temperature can lead to either increased, decreased or unchanged surface coverage. Provided that a critical minimum surface is maintained, wear and friction can be controlled. But once θ falls below this critical value, believed to be approx 0.5, friction and wear will rise. The adsorption of dilinoleic acid [4], a series of organic sulphur compounds [5] and a ZDDP (zinc dialkyldithiophosphate) [6] has been described in these terms.

3.4.2 Influence of Basestock

The model for film formation described above suggests that interactions between basestock and film-forming additives, which retard their adsorption, will have a detrimental influence on wear and friction. For instance, highly napthenic basestocks are good solvents for polar species whilst paraffinic basestocks are relatively poor solvents for polar species and will therefore enhance film-forming activity. Clear evidence of this effect has been shown for molybdenum chemistries [7] and for ZDDPs [8, 9].

3.4.3 Influence of Metal Surfaces

The two questions of interest here are:

(i) How does the chemical and structural nature of the metal surface influence the behaviour of additives in the control of friction and wear? and
(ii) Why are the chemical reactivities of rubbing surfaces higher than those of non-rubbing surfaces?

The mechanisms of film formation previously described involve both physical and chemical processes. It follows that factors favourable to film formation can influence friction and wear. Coefficients of friction were shown to vary from 0.04 for a reactive metal such as zinc, lubricated with 1% lauric acid, to 0.55 for an inert metal, silver, with the same lubricant [10]. These factors include strong dipole interactions or strong hydrogen bonding which aid physical adsorption and the ease of chemical reaction from this adsorbed layer. Both interactions favour the formation of low-shear-strength films and similar influences have been reported by many workers including wear for mixtures of dilinoleic and linoleic acids [11], and for ZDDPs [6].

As an illustration, Fig. 3.7 shows the influence of variations in steel metallurgy on the reaction between ZDDP and steels. Those steels such as stainless steel with high surface concentrations of inert oxides, e.g. Cr_2O_3, are much less reactive to ZDDPs and harder to lubricate than those such as ANSI52100 which have significant surface concentrations of reactive oxides, e.g. Fe_2O_3. The greater reactivity of pure iron is also shown.

Confirmation of this influence of surface oxide concentration is shown in Fig. 3.8, where an ANSI51200 disc has been exposed to a solution of radio-labelled ZDDP. A photographic film exposed to the disc shows areas of reacted film formation and areas where no film exists. Electron X-ray fluorescence shows that the inert areas are oxides of chromium and the reacted areas are oxides of iron.

Engineers tend to use increasingly harder metallurgies to combat abrasive wear whose surfaces are less and less reactive to anti-wear agents. Consequently the risk of adhesive wear increases. In addition, frictional heating can generate phase changes in steels, resulting in either hardening, e.g. PSATU3, or softening, EN32b, of components.

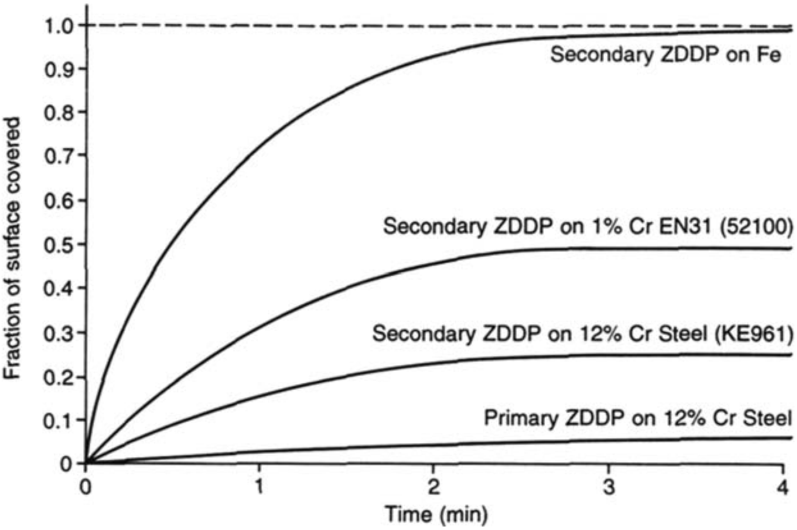


Fig. 3.7 ZDDP adsorption on ferrous surfaces: variations with steel metallurgy

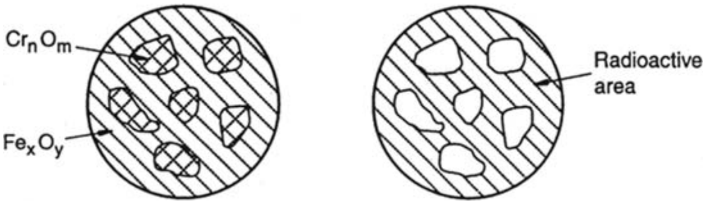


Fig. 3.8 Evidence for the inert nature of chromium oxides

Surfaces generated under rubbing conditions are more reactive towards additives than are static surfaces. In part this is due to the presence of oxide films on static surfaces which are removed by sliding contact and the fresh ‘nascent’ metal surface has a higher reactivity than its oxidised predecessor. In addition to the above, and of increasing interest, rubbing surfaces generate low energy, 1–3 eV, electrons or exoelectrons spontaneously [12], which can promote chemical reactions, i.e. polymerisation [13], and may be involved in the mechanism of ZDDP-reactive film formation [14].

3.4.4 Corrosive/Adhesive Balance

Wear control by reactive film formation involves a corrosive wear process to limit the rate of an adhesive wear process. The protective film is removed during the sliding process and must be replaced in time between successive contacts. If the rate of this corrosive film formation process is faster than required to control adhesion, then material loss, i.e. wear, will occur at an unacceptable rate. This excessive corrosion can occur either because the additive used is excessively reactive at the contact temperatures or because the concentration of the additive in the oils is too high. If the additive is present at too low a concentration to maintain film formation, then excessive adhesive wear will occur. Maintenance of this corrosive adhesive balance is essential and Fig. 3.9 shows the influence of anti-wear agents of differing chemical activity.

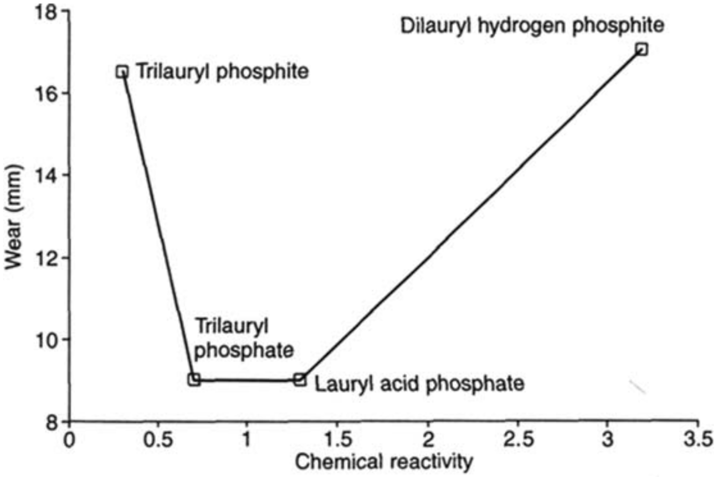


Fig. 3.9 The influence of anti-wear agents of differing chemical activities

3.5 Control of Friction and Wear by Various Classes of Compounds

The preceding sections have clearly shown that friction and/or wear may be controlled by a variety of classes of compounds which can form surface films. These compounds include:

(i) oxygen-containing organic compounds that have a polar head group capable of adsorption at surfaces. These include alcohols, esters and carboxylic acids,
(ii) organic compounds which contain nitrogen groups either in combination with (i) above or (iii) below,
(iii) organic sulphur compounds which can form reacted films at surfaces,
(iv) organic phosphorus compounds which can form reacted films at surfaces,
(v) organic boron compounds which *may* form reacted films at surfaces,
(vi) organic molybdenum compounds which can form MoS_2 film on surfaces,
(vii) ZDDPs which can form polymeric films on surfaces.

Within each of the above classes, additive structure interaction, operating environment, temperature, time and concentration will determine the effectiveness of each particular additive in its particular application.

3.5.1 Organic Oxygen Compounds

These compounds include esters, alcohols and acids and are the class of additives used to improve ‘oiliness’ and reduce friction. The carboxylic acids can function by forming metal soaps with the contacting surfaces. In this case there is evidence that the upper limit for friction reduction coincides with the melting point of the metal soap [10]. There is also evidence that control of chain length, chain matching of the carboxylic acid hydrocarbon backbone and choice of solvent hydrocarbon can minimise friction [10]. Figure 3.10 shows the influence of hydrocarbon backbone on friction of both carboxylic acids and alcohols.

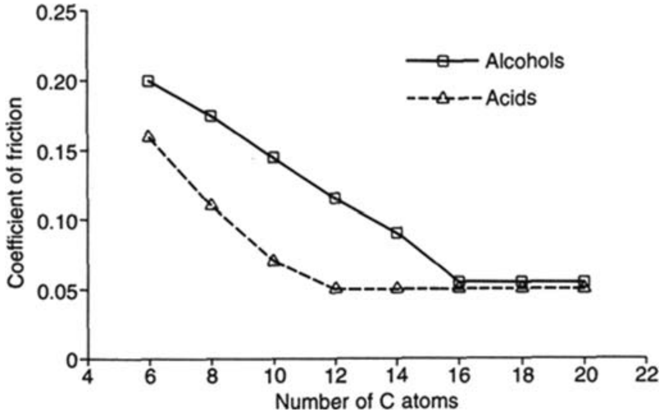


Fig. 3.10 The influence of hydrocarbon backbone carbon number on the friction of carboxylic acids and alcohols

Figure 3.11 shows the upper temperature limit of friction control for a homologous series of carboxylic acids in *n*-tetradecane. The peak at C = 14 shows the value of matching backbone chain length (and C–C bond angles) of additive and basestock.

The data points to the importance of two parameters, that of adhesive interactions between adsorbate and surface, and lateral interactions between adsorbate molecules on the surface. In general, the free energy of adsorption (at zero coverage) is of the order of 10–30 kJ mol^{-1} for alcohols, carboxylic acids and esters on ferrous surfaces, consistent with hydrogen bonding between surface and adsorbate.

Whilst polarity in a molecule is a prerequisite for adsorption, dipole moment measurements as a direct measure of polarity are not infallible predictors of friction

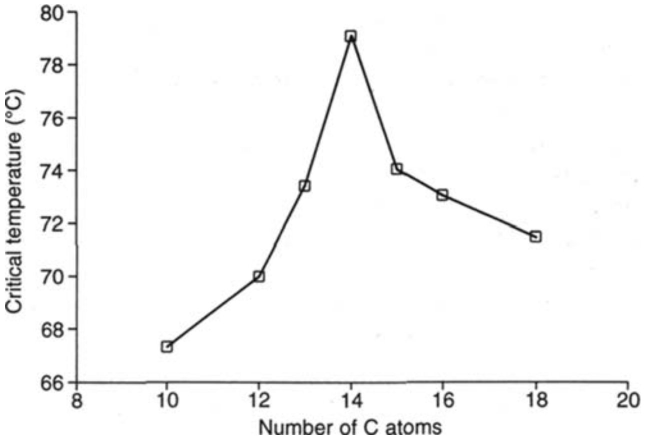


Fig. 3.11 The upper temperature limit of friction control for a homologous series of carboxylic acids in *n*-tetradecane

modification. For example, whilst nitroalkanes have greater dipole moments than carboxylic acids, 2.2 Debyes compared to 1.7 Debyes [15], they do not reduce friction under boundary conditions. The difference between the less polar groups of the known boundary lubricants and the nitro groups is that the former are capable of hydrogen bonding whereas the latter are not [16]. Hydrogen bonding is a special case of a donor–acceptor interaction with an electronegative atom, usually oxygen or nitrogen with an unshared electron pair, functioning as the acceptor and a hydrogen atom, covalently bonded to a second electronegative atom, functioning as the donor. Due to differences in electronegativity of the atoms comprising a hydrogen bonding functional group, as either donor or acceptor, hydrogen bonding groups must be polar, but the reverse is not necessarily true.

There has been debate for many years as to whether long-chain surfactant friction modifier additives reduce friction by forming adsorbed films of monolayer thickness or whether they form thick films equivalent to several, or many, multilayers [17]. An investigation compared a series of metal oleate friction modifier additives and their film-forming properties in rolling contact conditions using ultra-thin film interferometry. It was found that some of these additives form thick boundary films while others do not. It was concluded that thick boundary films result from the formation of insoluble iron(II) oleate on the rubbing surfaces and that for metal oleates this will occur only for metals lower than iron in the electrochemical series. This is due to a redox reaction involving iron from the steel surface and the metal oleate.

The behaviours of mono-, di- and triesters of glycerol oleate were compared as a range of commercial organic friction modifiers in a synthetic base fluid. Of the esters studied, the monoester gave the lowest friction and base fluid polarity had no discernable effect on boundary friction [18].

A recent study showed that under low-load conditions and with ultra-smooth surfaces, lyophilic friction modifiers can influence hydrodynamic friction by inducing slip at surfaces. Since the roughnesses necessary to observe this phenomenon are well below those of engineering surfaces, this has no relevance to current automotive applications of friction modifier-containing lubricants [19].

Most metal/oxide surfaces are partially hydroxylated in the presence of water vapour and can participate in hydrogen bonding either as a hydrogen atom donor or acceptor. Thus adsorption of hydrogen atom acceptors such as alkyl esters or compounds such as alcohols and carboxylic acids, which can act as either donors or acceptors, leads to friction reduction.

A high degree of lateral interaction forms a cohesive adsorbed layer which results in improved adsorption. Although this class of molecules is used in lubricants to reduce friction, they may also serve to reduce wear and protect against scuffing, particularly at low temperatures where ZDDP protective film formation rates are low.

The preceding section has been concerned with the formation of thin films, at most a few monolayers, at surfaces as a means of controlling friction. Tribopolymerisation reactions, to form thicker polymeric films at surfaces, are also possible and assist load bearing and increase surface separation by the lubricant [20]. These films can be formed by anionic-radical mechanisms [13]. The radicals are generated by low-energy (1–3 eV) exoelectrons [21], emitted spontaneously by solid surfaces when disturbed by plastic deformation, abrasion, fatigue cracking or phase transformation.

Film formation depends on the contact temperature and the structure of the monomer additive used. Low-temperature polymerisation is favoured where additional polymerisation occurs, e.g. by dialkyl phthalates. Condensation-type monomer polymerisation, e.g. C_{36} dimer acid/ethylene glycol esters, requires higher surface temperatures [22].

Films can be formed from dihydroxydocosanoic acid [23] and appear to be formed as polyesters by intermolecular dehydration to form a network polymer. In contrast, monohydroxydocosanoic acid gives a linear polymer. Coefficients of friction are not exceptionally low, with μ of the order of 0.1, but wear properties are claimed to be comparable or better than those of ZDDP, albeit only in simple FourBall testing. However, this mechanism of film formation may be applicable in very low or zero phosphorus formulations if the mechanisms for film generation are applicable in fully formulated oils.

3.5.2 Sulphur and Sulphur/Nitrogen Compounds

These classes of compounds were the first used during the industrial revolution to improve the performance of machinery and were developed to improve the scuffing load of gear lubricants. Examples of typical structures of sulphur/nitrogen compounds which have found application are given in Fig. 3.12.

Sulphur additives function by the formation of layers of FeS and $FeSO_4$ at ferrous surfaces where these films have a lower energy of adhesion to the substrate than to each other. The reaction of sulphur additives involves a controlled corrosion process;

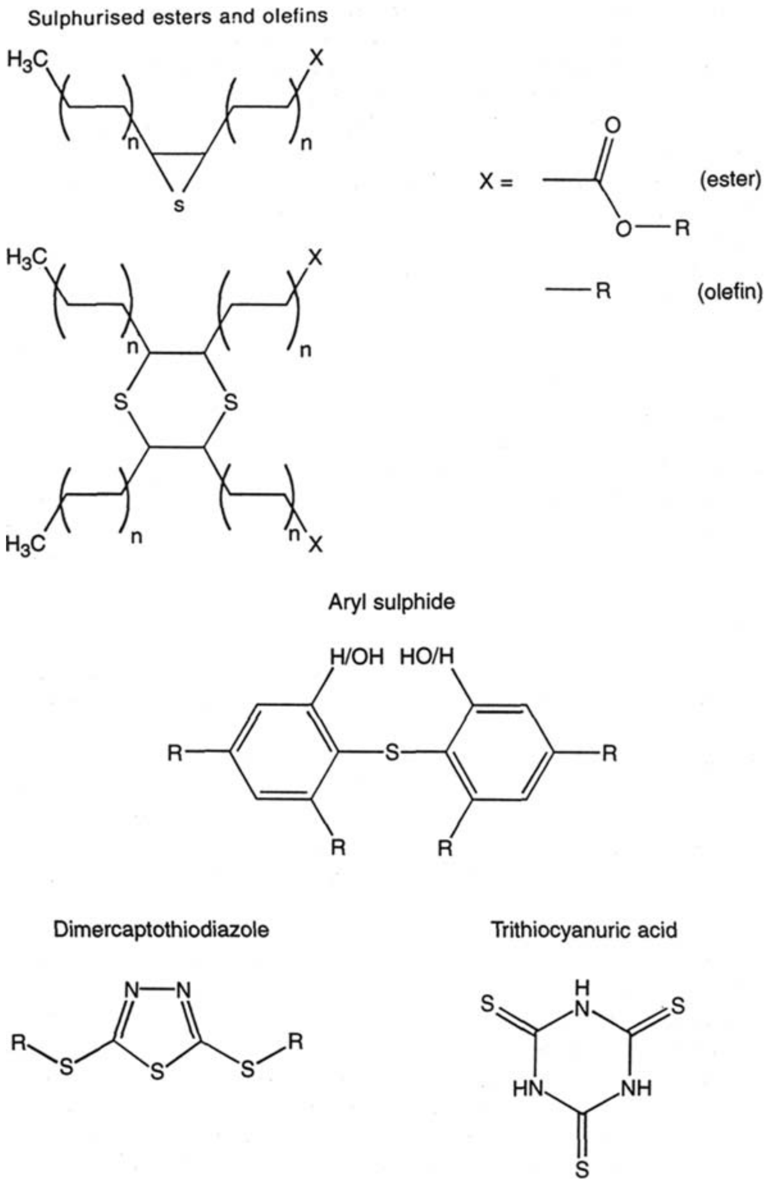


Fig. 3.12 Chemical structures of some typical sulphur and sulphur–nitrogen compounds

sulphurisation of the metal surfaces by the additive tends to occur at quite high surface temperatures. Therefore this type of additive has their principal application as extreme pressure, EP, additives in transmission fluids. Many of the more reactive species cause severe corrosion of copper-containing components such as bearings and this, plus the high temperatures needed to promote their film-forming reactions, has limited their usefulness in crankcase applications. Nevertheless, certain sulphur-containing compounds have been used as supplementary anti-wear agents in crankcase lubricants and have potential use in low or zero phosphorus application. Typical of these would be the sulphurised esters of fatty acids, the dimercaptothiadiazoles or the dithiocarbamates.

Dimercaptothiadiazoles are widely used as metal passivators and as load-carrying additives. They have been used particularly as potential replacements for ZDDPs in zero phosphorus formulations [24]. Structural features in the molecules can have considerable impact upon frictional and wear properties but appear to have little influence on rust inhibition and antioxidancy. In particular, the friction/wear properties may be modified by the side chains attached at the 2- and 5-carbon position of the thiadiazole ring. Particularly good friction and wear reduction occurs when a hydroxyl group is attached to the end of a straight alkyl chain. Side chains may contain phosphorus atoms and/or disulphide linkages, such as –S–S–P(S)(OR)$_2$, and –S–S–R. These phosphorus-containing derivatives exhibit extra effectiveness as friction modifiers and anti-wear agents. Surface films contain iron phosphate as well as FeS, polysulphide, $Fe_2(SO_4)_3$ and organonitrogen compounds found in the absence of phosphorus-containing substituents.

Dithiocarbamates of zinc, and particularly of molybdenum, show friction- and wear-reducing properties particularly when used in conjunction with ZDDPs and are discussed in the following sections.

3.5.3 Organophosphorus Esters

Organophosphorus esters have long been added to oils as anti-wear agents and mechanistic studies have identified two different types of reaction films:

- those derived from tricresyl phosphate, which form thin films, 0.1–2 nm, of low-shear-strength $FePO_4$ and Fe $PO_4.2H_2O$ and
- those which give thick, approx. 100–300 nm, films of a polymeric nature. These mainly consist of iron (III) monoalkyl/aryl phosphate oligomers, Fig. 3.13, of a type formed by phosphonates of the structure $(RO_2)_2P(O)H$, where R = hexyl, octyl, dodecyl, phenyl or octylphenyl [25].

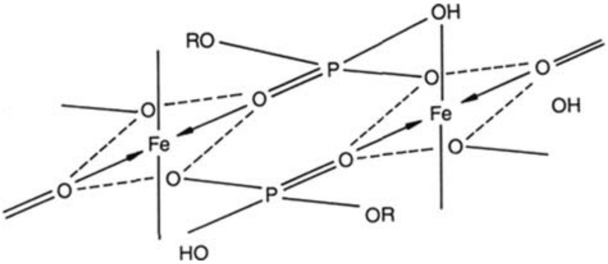


Fig. 3.13 The iron (III) monoalkyl/aryl phosphate oligomer

For tricresyl phosphate to be effective, oxygen, water and other polar impurities are important for the formation of reaction films. The beneficial influence of water and oxygen indicates that the formation of the reaction film is preceded by the hydrolysis of ester and the release of phosphoric acid which finally reacts with the surface oxide film. The importance of the polar impurities present in TCP has been demonstrated [26]; the probable identity of the important impurity is lauryl acid phosphate, found to be 20 times as effective at wear protection compared to pure tricresyl phosphate. A conclusion is that the ester function of phosphoric acid is necessary only to ensure solubility of the product in oil. TCP can also give rise to anti-rust protection by hydrolysis to phosphoric acid.

For various phosphonates, short-chain mono/dialkyl phosphonates, neutral amine salts of monoalkyl phosphonates and triiso-propyl phosphates form oily thin polymeric films because their physical properties do not encourage the retention of these films within the contact [27]. Long-chain-length mono- and dialkyl phosphonates form protective layers under boundary lubrication conditions. Monododecyl phosphonate yields films of approx. 100 μm thickness. The generation of these films depends on the availability of Fe^{3+} in the surface.

The film formation mechanism is believed to involve loss of an alkyl group by hydrolysis which generates two P–O ligands for co-ordination. The phosphate anion formed has reduced oil solubility, leading to accumulation in the boundary layer of oil covering the metal surface. The phosphonate anion reacts with $Fe^{(III)}$ created by oxidation in the rubbing contact by bridging rather than chelation. As polymer growth occurs the film graduates from being a soft viscous liquid to a glass-like solid. This film contributes to surface separation and hence reduces wear. All these phosphorus additives tend to produce their reaction films, either thin or thick, at surface temperatures lower than those required to form films from sulphur additives.

3.5.4 Molybdenum–Sulphur Compounds

Compounds such as MoDTC (molybdenum dithiocarbamate) or MoDDP (molybdenum dithiophosphate) react on surfaces to yield molybdenum disulphide. This compound has a hexagonal-type crystal structure where each molybdenum atom is surrounded at equal distances by six atoms of sulphur placed at the corners of a triangular right prism of 31.7 nm height. Each layer consists of two planes of sulphur atoms and an intermediate plane of molybdenum atoms. The distance between the planes of molybdenum and sulphur atoms is 15.8 nm. The bonds between molybdenum and sulphur are covalent whilst between the sulphur atoms the bonds are van der Waals type. The low binding energy between the planes of sulphur atoms allows molecular sliding along them. The shearing force further decreases due to lattice defects present in real crystals. The ease of shearing leads to unusually low coefficients of friction achievable with molybdenum additives, hence their excellent fuel economy, but environmental factors can be detrimental. Water and oxygen greatly influence film endurance, where small concentrations of oxygen oxidise surface layers to MoO_3, a hydrophilic layer which reduces the energy of adhesion between the crystals and the support surface. The oxidative dehydration of MoS_2, which can also involve S diffusion into ferrous surfaces, as well as the detrimental effect of water, explains in part why the good fuel economy achievable with molybdenum/sulphur oils is hard to sustain over long service periods. The friction reduction effect by molybdenum dithiocarbamate deteriorates with field service so that after 4000 miles no reduction in friction coefficient was seen relative to the base oil [28], although a significant proportion of the MoDTC was still in the oil. The use of antioxidants can inhibit the degradation of both MoDTC and ZDDP in oils and hence give improved sustainable fuel economy performance [29]. MoDTC does not form low-friction layers on its own but low-friction films are formed if ZDDP is present. A synergistic reduction in friction by ZDDP in conjunction with MoDTC has been demonstrated [30, 31].

Base oil composition can also influence the friction properties of MoDTC-containing oils, and hence the fuel economy benefits achievable by the use of this additive. Fuel economy in the ASTM Seq. VI test was improved between 0.8 and 1% by the addition of 1% MoDTC [7, 32]. Base oils with high VIs and/or high saturate levels were superior to ‘low-saturate’-level/low-VI base stocks in response to MoDTC and the differences were explained in terms of the effect of the base oil, as solvent, on adsorption of the MoDTC on the ferrous surfaces. It is reasonable to conclude that molybdenum/sulphur additive systems, when used with ZDDP-containing oils, lay down a layer of MoS_2 on top of a glass of ZDDP reaction products. The ZDDP layer acts as a source of sulphur, reduces oxidation of MoS_2, and limits diffusion of sulphur from MoS_2 into the ferrous substrate.

Both base oil properties, ZDDP structure and the antioxidancy of the oil, will influence both the frictional behaviour of the oil, its fuel economy performance and the degree to which this fuel economy benefit is sustained in service. Molybdenum-based oils are the best route yet available to deliver very low friction in service.

3.5.5 Metal–Phosphorus–Sulphur Additives – the ZDDPs

These additives have been used to enhance the boundary-lubricating properties of engine oils since the 1940s. Originally developed as antioxidants, it was soon recognised that they also acted to limit wear in both piston ring/liner and cam/follower situations. ZDDP reduces wear by forming relatively thick boundary lubrication films, of the order of 50–150 nm thick [33–35], and is based on a complex glass-like structure, Fig. 3.14, formed in rubbing tracks at contact temperatures lower than those required for the formation of thermal films. The rate of formation increases with temperature [36]. They do not develop under rolling contact conditions, nor when the hydrodynamic film thickness exceeds the surface roughness.

The composition of these glassy reaction films is variable, dependent upon contact conditions and oil formulation. The film is typically comprised of a glass of Zn, P and O and Mg and/or Ca with FeS or $FeSO_4$ as a separate phase. It appears that

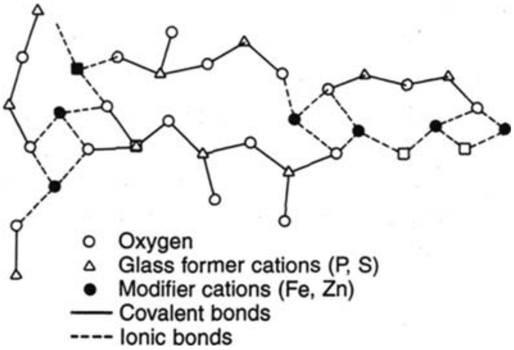


Fig. 3.14 Possible arrangements of atoms in ZDDP films

islands of film are formed on the steel surfaces, Fig. 3.15, which grow with time and/or temperature. These islands are believed to have a graded structure with a thin outer layer of zinc polyphosphate grading to a bulk film of pyro- or orthophosphate [37, 38].

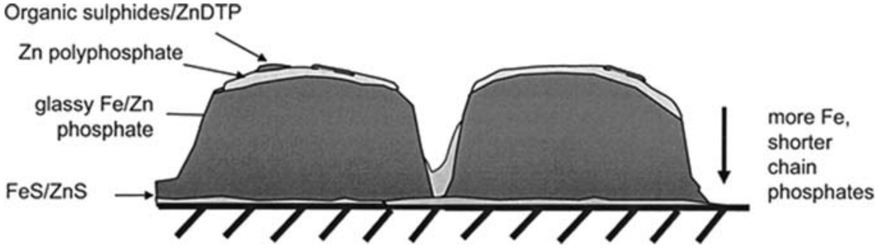


Fig. 3.15 Structure and composition of a ZDDP glass film

Under sliding conditions, films formed by ZDDPs behave in a plastic manner and boundary friction coefficients of ZDDP films are 0.13–0.15 [39]. In addition, they increase friction in the mixed lubrication region, secondary ZDDPs more so than primaries, which has an obvious impact upon energy efficiency. It may be that there is a thick viscous layer of organophosphate material on top of the solid reaction films but evidence for [40] is slightly weaker than the evidence against [41] and further studies are required to resolve this issue.

As for all additives, interactions with other additives in solution, Fig. 3.16, and competition for surface reaction sites together with the effect of environmental factors such as temperature, blow-by gases, water and fuel dilution have variable effects on the formation of the film. Because ZDDPs are much more widely used as anti-wear performance additives compared to other classes of compounds, these additive effects will now be discussed in greater detail than has been the case for other classes of anti-wear/friction additives. In particular the influence of structure, concentration, dispersant, detergent, antioxidancy and friction modifier on friction and wear will be discussed. In addition the influence of NO_x and H_2O will be briefly illustrated.

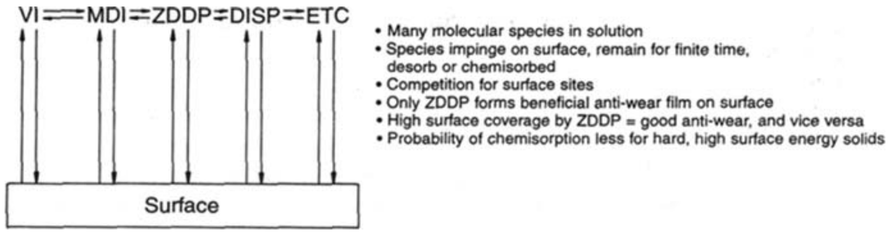
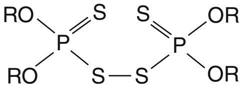


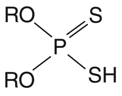
Fig. 3.16 ZDDP formation of anti-wear films

Most studies of the anti-wear properties of ZDDPs have concentrated on the influence of structure either on anti-wear activity or on mechanisms of film formation. For the former, nearly all experiments were conducted in rudimentary tribological tests and on solutions in simple base oils [42, 43]. The clear conclusion is that it is the structure of the alkyl groups that determines the anti-wear potency of the ZDDP. In particular, chain branching and chain length are critical such that short, branched-chain alkyl groups are more reactive than long primary alkyl chains. However, short-chain, primary alkyl groups can be more reactive than long-chain secondary ones. Similar considerations govern thermal stability [44], and there is an inverse relationship between the temperature of thermal decomposition and the potency of anti-wear protection. Commercial ZDDPs contain both the neutral $[(RO)_2P(S)S]_2Zn$ as both monomer and dimer, and the basic form as $[(RO)_2PS_2]_6Zn_4O$. The latter are more thermally stable than the former and are less effective as anti-wear film formers.

It follows from this that the ZDDPs which are most efficient at anti-wear film formation will also be likely to suffer depletion due to thermal effects. The thermal degradation of ZDDPs in service has often been confirmed by ^{31}P NMR and IR studies [45] and is not really important unless decomposition proceeds to the stage where significant reduction in phosphorus and sulphur levels as insoluble or volatile products occurs. Indeed, according to [6], the early stage decomposition products are:



and



which are equally effective as the parent ZDDP as anti-wear agents. It does mean, however, that under very high temperatures and/or very long drain service, the most active ZDDP may not give the best wear protection.

Figure 3.17 shows how high temperature affects the anti-wear protection of a passenger car engine oil formulation with a secondary ZDDP and with one based on primary ZDDP. The superior initial wear protection of the secondary ZDDP is destroyed much more quickly than that of the primary ZDDP oil. Blends of the two ZDDPs gave good initial wear protection and good sustained wear protection.

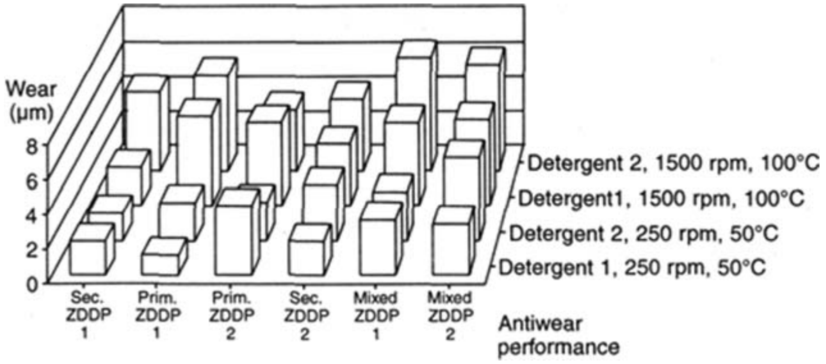
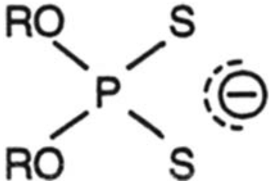


Fig. 3.17 Anti-wear performance versus speed, temperature and detergent

Thermal decomposition is initiated by a general migration of alkyl groups from oxygen atoms to sulphur atoms [46]. The rate of this reaction is governed by the ease with which nucleophilic substitution can take place at the α-carbon atom of the alkyl group. Steric hindrance by β-substituents to this nucleophilic attack also influences thermal stability.

The initial step of ZDDP reactions at surfaces involves the loss of Zn and the consequent formation of the nucleophilic species [6], Fig. 3.18:

Fig. 3.18 Nucleophile formed from ZDDP reaction at a surface

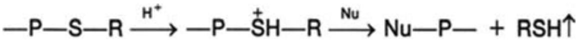


Nucleophilic attack by this species at the α-carbon atom will also be governed by the same steric considerations as in thermal decomposition and hence the inverse relationship of thermal stability and resistance to nucleophilic attack, and anti-wear activity and ease of nucleophilic attack. Further thermal processes involve olefin elimination from alkyl groups and lead to the formation of phosphorus acids. Nucleophilic substitutions of one phosphorus species by another leads to P–O–P structures and zinc mercaptide $Zn(SR)_2$ as a reaction intermediate. Reaction of this mercaptide with dithiophosphate leads to trithiophosphates and eventually tetrathiophosphates. Finally, an oil-insoluble deposit is formed of a mixture of zinc thiophosphate and zinc pyro- and polypyrothiophosphates.

3.5.5.1 The Influence of Neutral and Overbased Detergents

The rate of thermal decomposition of ZDDPs can be greatly inhibited by the presence of overbased detergents [47]. Inhibition of volatile alkyl thiol formation due to nucleophilic displacement of a protonated thioalkyl group was identified as the most probable mechanism of inhibition, Reaction (3.1), where PSR reacts with H^+ to produce PS^+HR which, in the presence of a nucleophile, produces NuP^+ and the volatile RSH:

Reaction 3.1 Inhibition of volatile thiol formation



$$-P-S-R \xrightarrow{H^+} -P-\overset{+}{S}H-R \xrightarrow{Nu} Nu-P- + RSH\uparrow$$

At lower temperatures, such as those for gasoline valve train wear tests where gross thermal decomposition does not occur, excessive overbasing leads to enhanced wear due to competition between the ZDDP and the surface-active detergent. This leads to reduced anti-wear film formation. At temperatures <100°C, competition between different detergents and ZDDPs for surface sites and solution interactions appear to be very specific. Figure 3.17 shows the results of valve train wear tests carried out with Mg and CaHBNS (high base number sulphonates) at 50 and 100°C with a range of ZDDPs for the same TBN and phosphorus level. From this it can be clearly seen that although the general structural/activity relationships appear to hold, important and unexpected exceptions, both good and bad, occur – so that whilst in general CaHBNS is superior to MgHBNS oils, a secondary ZDDP gives better wear protection with MgHBNS than one would expect from its alkyl group structure. Low base number sulphonates also influence wear in a manner which is temperature dependent.

3.5.5.2 Influence of Dispersants

Strong solution interactions between dispersants of the PIBSA/PAM type and ZDDPs are well documented [48, 49]. These interactions are claimed to involve either hydrogen bonding between the – R_2NH groups of the dispersant (R = H or alkyl) and –P=O, –P=S, –P–O–H and –P–S–H groups of ZDDP and decomposition products [50], or direct bonding of zinc atoms of ZDDP to nitrogen donor ligands [51], the latter carried out with 2,2-bipyridine and *N*,*N*-diethylethylenediamine, where isolatable 1:1 complexes are formed. These complexes are unlikely to be formed by dispersants since co-ordination around Zn atoms is less likely.

It was also shown that PIBSA/PAM-type dispersants were able to convert basic (more thermally stable) ZDDP to normal (more active) forms [52]. Thus dispersants in general are expected to be beneficial for wear protection and it has been demonstrated that succinimide dispersants can partially remove films formed by ZDDP under rubbing conditions [53]. It is not known whether or not the dispersant used was borated, which may influence this phenomenon significantly.

The benefit of dispersants of different molecular weight and functionality can be seen from a number of studies but many of them are complicated by neglecting the influence of dispersant upon viscosity and hence oil film thickness. However, under boundary lubrication conditions, dispersants improve the wear protection of a secondary ZDDP, from which it may be reasonably presumed for other ZDDPs, at both high and low temperature/speed combinations. There is some evidence that boration of dispersants improves wear, especially at low temperatures, possibly due to a reduced complexation of ZDDP in solution by the more ‘active’ amine groups. ‘Optimum (0.13) zinc/dispersant nitrogen ratios’ have been reported for wear control as the best compromise between basic to neutral for ZDDP conversion, solution complexation and surface active site competition [54]. It is also well outside the range of dispersant nitrogen to zinc ratios encountered in current formulations, typically in the range of 0.06–0.010. In addition to influencing wear protection by ZDDPs, dispersants also reduce engine wear arising from soot abrasion or lubricant thickening in diesel engines.

3.5.5.3 Influence of Antioxidants

Oxidation of base oil in a free radical process in solution can be represented by the following series of reactions, Reaction sequence (3.2(i–vii)) [55]:

$$\begin{array}{lll}
\mathrm{RH} + \text{e.g. } \mathrm{NO_2} \rightarrow \mathrm{R^\bullet} + \mathrm{H^\bullet} & \text{(i)} & \text{Initiation} \\
\mathrm{R^\bullet} + \mathrm{O_2} \rightarrow \mathrm{ROO^\bullet} & \text{(ii)} & \text{Propagation} \\
\mathrm{ROO^\bullet} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R^\bullet} & \text{(iii)} & \\
\mathrm{ROO^\bullet} + \mathrm{ROO^\bullet} \rightarrow \text{Inactive product, Termination} & & \\
\mathrm{R^\bullet} + \mathrm{ROO^\bullet} \rightarrow \mathrm{ROOR} & \text{(iv)} & \\
\mathrm{R^\bullet} + \mathrm{R^\bullet} \rightarrow \mathrm{RR} & \text{(v)} & \\
\text{Chain branching occurs via:} & & \\
\mathrm{ROOH} \rightarrow \mathrm{RO^\bullet} + \mathrm{OH^\bullet} & \text{(vi)} & \\
\mathrm{2ROOH} \rightarrow \mathrm{RO^\bullet} + \mathrm{ROO^\bullet} + \mathrm{H_2O} & \text{(vii)} &
\end{array}$$

Inhibition of oxidation occurs by the prevention of chain propagation, Equation (3.2) (ii) or (iii). Hindered phenols and aromatic amines donate a hydrogen atom to the peroxy radical, ROO$^\cdot$, Reaction (3.3), in successful competition with Reaction (3.2(iii)):

$$\mathrm{ROO^\bullet} + \mathrm{AH} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{A^\bullet} + \mathrm{RH} \qquad \text{(Reaction 3.3)}$$

A$^\bullet$, the antioxidant radical is stabilised by resonance and is hence incapable of abstraction of a hydrogen atom from RH as required in Reaction (iii) and the chain reaction is thereby broken. Frequently A$^\bullet$ radical will react with another radical, ROO$^\bullet$ or A$^\bullet$, to give a stable end product.

ZDDPs, and also metal dithiocarbonates, act as oxidation inhibitors by peroxide decomposition in a manner which does not produce radicals, thus removing a major initiation source. It seems likely that ZDDPs are sources of DDPAs (dialkyldithiophosphonic acids) and it is this which is responsible for either ionic decomposition of the hydroperoxide or decomposition by electron transfer, Reaction (3.4) [56]:

$$[\mathrm{(RO)_2PS_2}]\mathrm{H} \rightarrow [\mathrm{(RO)_2PS_2}]^- + \mathrm{H^+} \qquad \text{(Reaction 3.4)}$$

Reaction products include disulphides $[(RO)_2PS_2]_2$ as a major product as well as the monosulphide, $[(RO)_2PS]_2S$, and the trisulphide, $[(RO)_2PS_2]_2S$ [57]. Oxidation of ZDDP by hydroperoxide, studied by Raman and ^{31}P NMR spectroscopy, was shown to involve a first stage of neutral ZDDP oxidation to a basic form. It is this form which is then oxidised to other products by loss of the $(RO)_2PS_2$ coordinating group [58]. It is clear that if a ZDDP molecule is acting as an antioxidant, then it cannot act as an anti-wear film-forming agent at the same time. Therefore wear protection will be reduced or conversely, if the ZDDP is protected from oxidation by using alternative antioxidants, the overall anti-wear performance of the lubricant may be improved. Inhibition of peroxide formation, Reaction (3.2(ii)), is very difficult because of the high rate constant value, 10^8 1 mol^{-1} s^{-1} [59]. Zinc dialkyldithiocarbamates are alternative peroxide radical scavengers and like the usual antioxidants, sterically hindered phenols and aromatic amines, they terminate peroxide radicals by Reaction (3.3).

Of this latter group, the most effective inhibitors of high-temperature oxidation are claimed to be the aromatic amines [56], but these are capable of complexing ZDDPs and hence inhibiting their anti-wear performance. Careful balance of ZDDP and antioxidant(s) is required to achieve both wear and viscosity increase control.

3.5.5.4 Influence of Combustion Products on Wear Protection by ZDDPs

Combustion of hydrocarbon fuels forms products which can greatly influence the anti-wear protection of ZDDP. Principal amongst these are water, and oxides and oxyacids of nitrogen and sulphur. Together with unburned fuel, these are the key constituents of blow-by gases that can interact with the lubricant on cylinder liners, in the crankcase and in the valve train areas. Significant dilution by unburned fuel occurs under low temperature/speed conditions which, in addition to producing sludge, results in a significant viscosity decrease, leading to reduced lubricant film thicknesses in contacts and hence increased rates of wear [60]. Water levels in engine lubricants under low temperature/low speed running conditions can reach very high levels such as 11% under the conditions used in the Mercedes-Benz HKL Test and it may also be approached in the ultra-low-temperature phase of the Mercedes-Benz M111 Sludge and Wear Test.

How the condensed water influences wear is largely determined by the ability of the detergent/dispersant system to emulsify the water. Stable emulsions have small droplet sizes and these give rise to less wear than when unstable emulsions with larger droplet sizes are formed [61]. Wear occurs by corrosive oxidation and partition of ZDDP into the aqueous phase does not occur. Detergent systems which formed unstable emulsions gave rise to high levels of wear, whilst those which gave rise to stable emulsions gave low levels of wear. These effects can mask the normal ZDDP/structure relationships.

3.5.5.5 Oxy Acids of Nitrogen and NO_x

These combustion products are strong pro-oxidants and in addition to their role in viscosity increase and sludge formation [62], they have a marked influence on rates of wear, especially of the valve train [62, 63]. Introduction of NO_x at a rate of 0.008 m^3s^{-1} at 2000 ppm into the crankcase of a 2-l Nissan OHC engine during a motored test increased cam nose wear by 1.6 times over the same test with no NO_x. This agrees with general experience from motored cylinder head rig tests. Since NO_x and nitrous acids are strong oxidising agents, they cause both local, in contact area, and general, in crankcase, depletion of ZDDP with consequent increases in wear rate.

3.5.5.6 Effect of Soot on Wear Protection by ZDDPs

Fuel combustion can lead to pyrolysis of hydrocarbon fuels and soot formation, important in diesel engines and contributing to particulate emissions. A proportion of this soot finds its way into the lubricating oil and increasing use of EGR systems to reduce particulate and gaseous emissions has led to higher levels of soot loading in lubricants.

Concern amongst vehicle manufacturers about the impact of soot on durability has led to the development of engine tests to evaluate the lubricant's ability to control its detrimental effects. Such tests are the USA Mack T8 test and the European PSA XUD11ATE/L test. This latter test was developed because increasing soot levels due to the use of EGR could cause increased levels of engine wear [64], in addition to increased oil viscosity due to soot agglomeration.

Colloidal sols of soot are entrained into the contact at slow entrainment speeds and they detrimentally influence the film characteristics of oils [65]. It was also shown, not surprisingly, that this entrainment is more pronounced at high temperatures.

3.6 Overall Summary

Control of adhesive wear requires the formation of thick reacted chemical films at the surfaces. They have lower shear strength than the metal surface and hence are removed, partially or fully, during sliding. Replacement of these films during the 'out-of-contact' time of the surfaces is essential for the control of wear. Because this process is a form of corrosive attack of the surfaces, careful control of chemical activity and additive concentration are needed if catastrophic corrosive wear is to be minimised.

Thick films, however, are associated with relatively high coefficients of friction. Those additives which are effective at reducing friction are:

(i) organic molecules which form relatively thin films and
(ii) inorganic solids such as MoS_2 which form planar layers of low shear strength on the surface.

Both low friction and low wear can be achieved if these films of friction modifier are laid down on thicker films of, say, ZDDP. The anti-wear and friction properties of several classes of additives have been described together with the influence of structure. In the case of ZDDP, the role of other additives on film formation and anti-wear behaviour has been discussed. Successful control of anti-wear and anti-friction properties of oils requires a careful balance of the additives in the formulation.

Problems of formulating low-sulphur and -phosphorus lubricants: The need for engine manufacturers to ensure the durability of exhaust after-treatment devices, and hence to maintain exhaust emission standards, has led to a demand for crankcase lubricants which contain reduced levels of sulphur and phosphorus. These elements are implicated in the reduction in efficiency of such after-treatment devices.

A major source of sulphur in most engine oils is the base stock into which the additive package is blended. These base oils are also used as diluents for highly viscous lubricant additives in order to facilitate handling and blending. For this reason it is likely that low-sulphur and -phosphorus formulations will be blended using expensive, non-polar, Group IV basestocks such as poly-α-olefins, together with, perhaps, some polar ester to improve the solubility of the additive package used. These basestocks have excellent low-temperature viscometric properties and allow the blending of oils with a wide viscosity range. These basestocks also have lower values of limiting traction coefficients than do iso-viscous, higher sulphur Groups I–III basestocks. This property is associated with improved fuel efficiency.

The downside is that these base oils have lower values of pressure viscosity coefficients and hence under both hydrodynamic and elastohydrodynamic lubrication conditions, the films formed in contacts will be thinner than that for an iso-viscous, higher sulphur basestock.

The principal problem, which is compounded by the above, is that the most cost-effective source of anti-wear film formation and the most effective peroxide decomposing agent has, since the 1940s, been ZDDPs which contain both sulphur and phosphorus as the active elements.

An enforced reduction in the concentration of ZDDPs and MoS compounds which can be included in additive packages for low SAPs applications means that consideration must be given to how to maintain wear protection and antioxidancy at an acceptable level. Normal phosphorus levels are of the order of 0.12% in the finished, formulated lubricant. If levels of 0.08% phosphorus are required, then this poses few problems since such formulations have already been well tried in certain markets. If levels of 0.05% phosphorus are stipulated, then formulating to meet wear targets becomes more difficult and interactions between ZDDPs and other additives present as well as surface competition between additives become critical.

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Chapter 4
Oxidative Degradation and Stabilisation of Mineral Oil-Based Lubricants

G. Aguilar, G. Mazzamaro and M. Rasberger

Abstract Thermally induced hydrocarbon oxidation is a self-accelerating autoxidation process and is divided into 'low'-, 30–120°C, and 'high'-, >120°C, temperature phases. The first has four stages – induction of radical chain reactions, propagation, branching and then termination. Mechanisms of these processes are described and discussed. Differences in hydrocarbon reactivity are related to molecular structure. For hydrocarbon oxidation >120°C, the first stage is the same as low-temperature oxidation but with reduced selectivity and increased reactivity; second, the oxidation phase becomes diffusion controlled as hydrocarbon viscosities increase from progressive polycondensation of higher molecular weight products, causing varnish and sludge formation. Base oil oxidation stabilities depend upon their derivation, whether solvent neutral, hydrocracked or synthetic, and their response to antioxidant treatment. Lubricant oxidation control focuses on radical scavengers and hydroperoxide decomposers and their synergistic mixtures.

Engine oils increasingly use phenolic and aminic antioxidants as radical scavengers with organometallic complex antioxidants. Sterically hindered phenols substituted at 2- and 6-positions by *t*-butyl groups are particularly effective, reacting successively with peroxy radicals to form stable cyclohexadieneone peroxides. Secondary amines as either two aryl or phenyl and naphthyl groups are very effective at eliminating four peroxy radicals per molecule. They are more effective by a ratio of 4:2 than the sterically hindered phenols below 120°C. At higher temperatures a catalytic cycle is suggested as an extended stabilisation mechanism. Transition metal ions with two valence states, $Fe^{2+/3+}$, $Cu^{1+/2+}$, etc. as trace quantities of metal soaps catalyse/retard autoxidation according to concentration and/or combination of metals. They catalyse or inhibit oxidation by complexing and decomposing hydroperoxides or can also oxidise peroxy radicals and reduce alkyl radicals to inert products. Organomolybdenum complexes such as molybdenum dialkyldithiocarbamates, MDTC, are increasingly used to stabilise engine lubricants particularly because of synergy with other antioxidants such as alkylated diphenylamines.

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4.1 Introduction

Reactions of oxygen with most organic materials are important from an economical and ecological standpoint. Processes such as the biological O_2/CO_2 cycle, the targeted oxidation of defined organic molecules, or the enzymatic oxidation of waste are all useful reactions. In contrast, reactions of atmospheric oxygen with hydrocarbon polymers and liquid hydrocarbons (lubricants), as well as with certain biological systems, under varying conditions of temperature and oxygen pressure are undesirable processes. Such reactions lead to deterioration of these materials. All oxidative processes with oxygen have a common reaction pattern attributable to the biradical status of oxygen.

This contribution presents the degradation reaction mechanisms and processes of lubricants and the factors influencing them. In addition, mechanisms by which antioxidants inhibit lubricant oxidation with respect to specific industrial and engine oil applications are suggested.

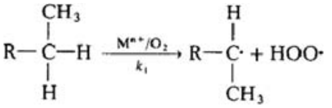
4.2 Autoxidation of Hydrocarbons

4.2.1 Oxidation of Hydrocarbons at Low Temperature (30–120°C)

The self-accelerating oxidation of hydrocarbons is called autoxidation. Its initial stage is characterised by a slow reaction with oxygen followed by a phase of increased conversion until the process comes to a standstill. The degradation is driven by an autocatalytic reaction described by the well-established free radical mechanism [1, 2], consisting of four distinct stages:

- initiation of the radical chain reaction,
- propagation of the radical chain reaction,
- chain branching,
- termination of the radical chain reaction.

Initiation of the radical chain reaction: Under normal conditions, i.e. moderate temperature and oxygen partial pressure greater than 50 torr, the first step is a process catalysed by traces of transition metal ions, Reaction (4.1) [3]:



$$R-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-H \xrightarrow[k_1]{M^{n+}/O_2} R-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}\cdot + HOO\cdot$$

(Reaction 4.1)

R refers to a long-chain alkyl substituent and the catalyst M^{n+} is a transition metal such as Co, Fe, V, Cr, Cu or Mn. The rate of initiation is very slow, the rate constant $k_1 = 10^{-9}$–$10^{-10}\,\mathrm{l\,mol^{-1}s^{-1}}$ [4, 5]. The site of the oxygen attack is determined by the strength of the C–H bond, and the reactivity for hydrogen abstraction increases in the following order given below; hence, oxidation of an *n*-paraffin normally commences by abstraction of a hydrogen at the second carbon atom (α-position to the CH group).

$$RCH_2{-}H < R_2CH{-}H < R_3C{-}H < RCH{=}CH(R)HC{-}H < C_6H_5(R)HC{-}H$$

Propagation of the radical chain reaction: Once an alkyl radical has been formed, this reacts irreversibly with oxygen to form an alkyl peroxy radical, Reaction (4.2), which is extremely fast, $k_2 = 10^7\text{–}10^9$ l mol^{-1}s^{-1}, and has a very low activation energy; k_2 is independent of temperature.

$$R(CH_3)CH\cdot + O_2 \xrightarrow{k_2} R(CH_3)CH{—}OO\cdot \qquad \text{(Reaction 4.2)}$$

The rate of reaction of carbon-centred radicals with oxygen depends on the type of substituents attached to the C atom and increases in the following order given below. For instance, a tertiary alkyl radical reacts 10 times faster with oxygen than does a methyl radical. This difference in reactivity explains why hydrocarbons with tertiary hydrogens (iso-paraffins) are oxidised faster than *n*-paraffins:

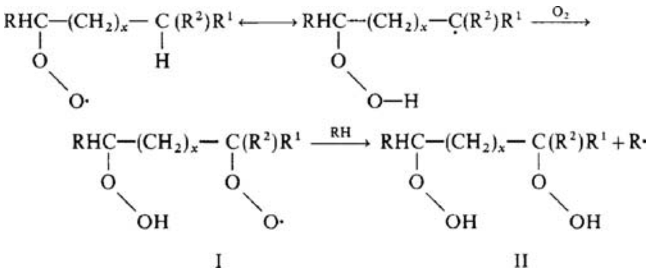
$$H_3C\cdot < C_6H_5(R)CH\cdot < RCH{=}CH(R)CH\cdot < R_2CH\cdot < R_3C\cdot$$

The next step in the chain propagation scheme is the hydrogen abstraction by a peroxy radical from another hydrocarbon, Reaction (4.3):

$$R(CH_3)CHOO\cdot + RH \xrightarrow{k_3} R(CH_3)CHOOH + R\cdot \qquad \text{(Reaction 4.3)}$$

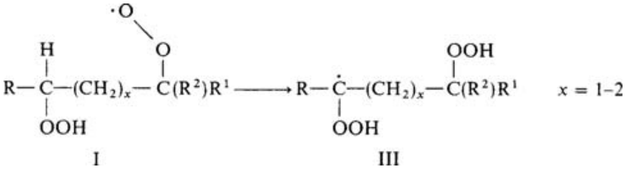
This leads to a hydroperoxide and an alkyl radical, which can again react with oxygen according to Reaction (4.2). The rate of Reaction (4.3) is slow, $k_3 = 10^{-1}{-}10^{-5}\,\text{l mol}^{-1}\text{s}^{-1}$at 30°C, dependent on the type of hydrocarbon, when compared with Reaction (4.2), and is therefore the rate-determining step for chain propagation. Due to their low reactivity, peroxy radicals are present in relatively high concentration in the system when compared with other radicals, determined via electron spin resonance.

Since peroxy radicals possess a low energy status, they react selectively and abstract tertiary hydrogen atoms in preference to secondary and primary hydrogen atoms with relative rates of 1:30:300 for C–H primary:C–H secondary:C–H tertiary [6]. Their reactivity is also influenced by steric effects: primary and secondary peroxy radicals show a three to five times higher reactivity than tertiary peroxy radicals [7]. A more favourable route of hydrogen abstraction by a peroxy radical [8–10] occurs via an intramolecular propagation outlined in Reaction sequence (4.4), where x is equal to 1 or 2, R^1 is a terminal alkyl group and R^2 hydrogen or an alkyl group.



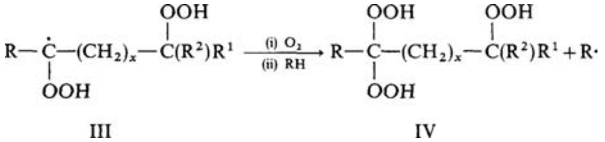
(Reaction Sequence 4.4)

The hydroperoxide–peroxy radical (I) reacts with hydrocarbons through intermolecular hydrogen radical abstraction, resulting in an alkyl dihydroperoxide (II) and a chain-initiating alkyl radical. Radical (I) may also intramolecularly abstract a hydrogen radical, Reaction (4.5):



(Reaction 4.5)

The alkyl dihydroperoxide radical (III) may then react with oxygen, followed by additional intermolecular hydrogen abstraction to yield an alkyl trihydroperoxide (IV) and an alkyl radical, Reaction (4.6):



$$\mathrm{R{-}\dot{C}(OOH){-}(CH_2)_x{-}C(OOH)(R^2)R^1} \xrightarrow[\text{(ii) RH}]{\text{(i) }\mathrm{O_2}} \mathrm{R{-}C(OOH)_2{-}(CH_2)_x{-}C(OOH)(R^2)R^1 + R\cdot}$$

(Reaction 4.6)

The occurrence of these intramolecular reaction sequences leads to an increased rate of formation of hydroperoxide, which results in a reinforced autocatalytic degradation of the hydrocarbons.

Chain branching: During the early stage of autoxidation, various types of hydroperoxides are generated. At low concentrations they may be cleaved homolytically to yield an alkoxy and a hydroxy radical, Reaction (4.7):

$$\mathrm{ROOH} \xrightarrow{k_7} \mathrm{RO\cdot + HO\cdot} \qquad \text{(Reaction 4.7)}$$

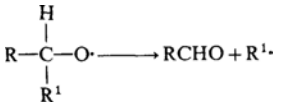
However, this process is thwarted because of a high activation energy; hence, Reaction (4.7) plays a significant role at higher temperatures or under catalysed conditions, considered in Sections 4.2.2 and 4.2.3. Once formed, hydroxy and especially primary alkoxy radicals are so active that they abstract hydrogen atoms in non-selective reactions, Reactions (4.8–4.10):

$$HO\cdot + CH_3{-}R \rightarrow H_2O + RCH_2\cdot \qquad \text{(Reaction 4.8)}$$

$$HO\cdot + R{-}CH_2{-}R^1 \rightarrow H_2O + R(R^1)HC\cdot \qquad \text{(Reaction 4.9)}$$

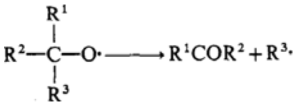
$$RCH_2O\cdot + CH_3{-}R \rightarrow RCH_2OH + RH_2C\cdot \qquad \text{(Reaction 4.10)}$$

Secondary and tertiary alkoxy radicals prefer to form aldehydes, Reaction (4.11), and ketones, Reaction (4.12):



$$R{-}\overset{H}{\underset{R^1}{C}}{-}O\cdot \longrightarrow RCHO + R^1\cdot$$

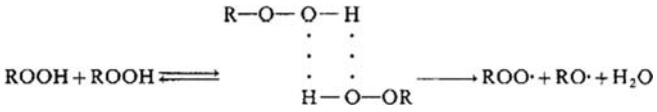
(Reaction 4.11)



$$R^2{-}\overset{R^1}{\underset{R^3}{C}}{-}O\cdot \longrightarrow R^1COR^2 + R^3\cdot$$

(Reaction 4.12)

At high concentrations, i.e. at an advanced state of oxidation, hydroperoxides may react via a bimolecular mechanism, Reaction (4.13):



$$ROOH + ROOH \rightleftharpoons \begin{matrix} R{-}O{-}O{-}H \\ \vdots \quad \vdots \\ H{-}O{-}OR \end{matrix} \longrightarrow ROO\cdot + RO\cdot + H_2O$$

(Reaction 4.13)

As a consequence of hydroperoxide accumulation and subsequent cleavage, the concentration of reactive free radicals initiating new chains increases. The time from the beginning of the oxidation to the autocatalytic phase of the autoxidation is called the ‘induction period’. The relationship between hydroperoxide accumulation and oxygen uptake of a hydrocarbon is schematically presented in Fig. 4.1. As can be seen, during the induction period, hydroperoxides are accumulated; after the induction period, the oxidation is autocatalysed.

Termination of the radical chain reaction: As the reaction proceeds, autoxidation is followed by an autoretardation stage, resulting in a standstill before the hydrocarbon is completely consumed. This autotermination is called the ‘chain termination reaction’ and dominates in this final phase of the oxidation process such that degradation comes to a halt. Termination may be effected by the combination of radical species such as peroxy radicals to yield ketones and alcohols, Reaction sequence (4.14):

$$\begin{aligned} &2RR^1CHOO\cdot \longleftrightarrow [R(R^1)CHOOOOCH(R^1)R] \\ &\rightarrow R(R^1)C{=}O + O_2 + HO{-}CH(R^1)R \end{aligned} \qquad \text{(Reaction Sequence 4.14)}$$

In this example, primary and secondary peroxy radicals form intermediates which disproportionate to non-radical degradation products. In contrast, tertiary peroxy radicals may either combine to give di-tertiary alkyl peroxides or undergo a

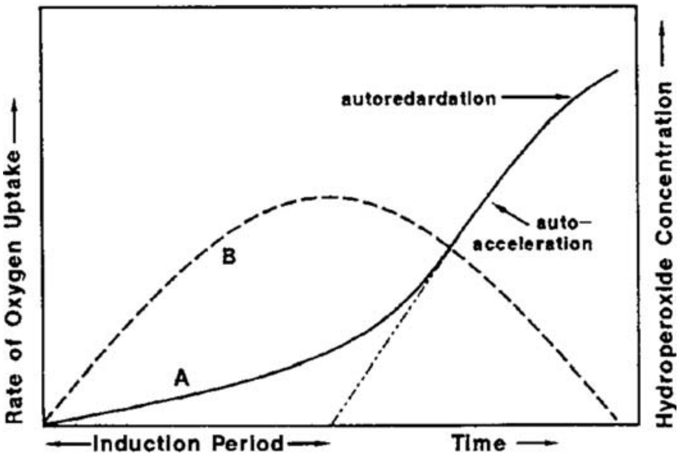
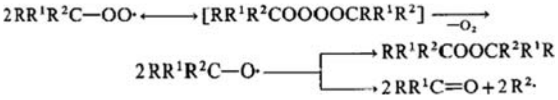


Fig. 4.1 Influence of hydroperoxide concentration on the rate of oxygen uptake over time; A = rate of oxygen uptake; B = hydroperoxide concentration (a schematic drawing only)

cleavage reaction leading to ketones and alkyl radicals, Reaction sequence (4.15). Generally, the rate of termination increases across the series: tertiary peroxy < secondary peroxy < primary peroxy.



$$2RR^1R^2C{-}OO\cdot \longleftrightarrow [RR^1R^2COOOOCRR^1R^2] \xrightarrow[-O_2]{} 2RR^1R^2C{-}O\cdot \begin{cases} \rightarrow RR^1R^2COOCR^2R^1R \\ \rightarrow 2RR^1C{=}O + 2R^2\cdot \end{cases}$$

(Reaction Sequence 4.15)

If the oxygen concentration in the bulk liquid phase is limited, for an oxygen partial pressure below 50 torr, two additional ways of radical recombination result, Reactions (4.16) and (4.17):

$$R\cdot + ROO\cdot \rightarrow ROOR \qquad \text{(Reaction 4.16)}$$

$$R\cdot + R\cdot \rightarrow R{-}R \qquad \text{(Reaction 4.17)}$$

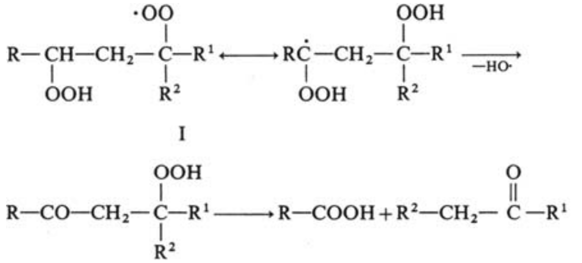
In summary, the uncatalysed oxidation of hydrocarbons at temperatures of up to 120°C leads to alkylhydroperoxides, ROOH, dialkylperoxides, ROOR, alcohols, ROH, aldehydes, RCHO and ketones, $RR^1C{=}O$. In addition, cleavage of a dihydroperoxide II of Reaction (4.4) leads to diketones, $RCO(CH_2)_xCOR^1$, ketoaldehydes, $RCO(CH_2)_xCHO$, hydroxyketones, $RCH(OH){-}(CH_2)_xCOR^1$, and so forth. Under metal-catalysed conditions or at higher temperatures, considered in Sections 4.2.2 and 4.2.3, degradation leads to a complex mixture of final products.

4.2.2 Oxidation of Hydrocarbons at High Temperature (>120°C)

Above 120°C the degradation process can be divided into a primary and a secondary oxidation phase.

Primary oxidation phase: Initiation and propagation of the radical chain reaction are the same as discussed under low-temperature conditions, but selectivity is reduced and reaction rates increased. At high temperature the cleavage of hydroperoxides plays the most important role.

Reaction (4.7) leads to a proliferation of hydroxy radicals, which non-selectively abstract hydrogen atoms, see Reactions (4.8) and (4.9). Acids are formed by the following two reactions, which start from a hydroperoxy–peroxy radical, see Reaction (4.4), and an aldehyde [9, 10]. Carboxylic acids (RCOOH), formed according to Reaction sequences (4.18) and (4.19), represent one of the principal products under these oxidation conditions. In a subsequent step they can react with alcohols R^1OH, produced by Reactions (4.10) and (4.14), to form esters, $RCOOR^1$. In addition, when the rate of oxidation becomes limited by diffusion, ethers are formed, Reaction sequence (4.20):

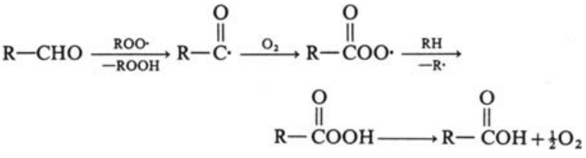


$$R-\underset{OOH}{CH}-CH_2-\overset{\cdot OO}{\underset{R^2}{C}}-R^1 \longleftrightarrow R\underset{OOH}{\dot{C}}-CH_2-\overset{OOH}{\underset{R^2}{C}}-R^1 \xrightarrow[-HO\cdot]{}$$

I

$$R-CO-CH_2-\overset{OOH}{\underset{R^2}{C}}-R^1 \longrightarrow R-COOH + R^2-CH_2-\overset{O}{\overset{\|}{C}}-R^1$$

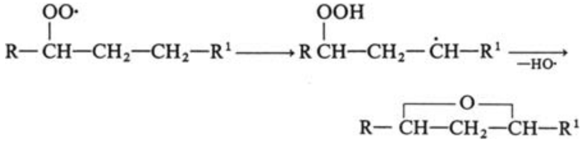
(Reaction Sequence 4.18)



$$R-CHO \xrightarrow[-ROOH]{ROO\cdot} R-\overset{O}{\overset{\|}{C}}\cdot \xrightarrow{O_2} R-\overset{O}{\overset{\|}{C}}OO\cdot \xrightarrow[-R\cdot]{RH}$$

$$R-\overset{O}{\overset{\|}{C}}OOH \longrightarrow R-\overset{O}{\overset{\|}{C}}OH + \tfrac{1}{2}O_2$$

(Reaction Sequence 4.19)



$$R-\overset{OO\cdot}{CH}-CH_2-CH_2-R^1 \longrightarrow R\,\overset{OOH}{CH}-CH_2-\dot{C}H-R^1 \xrightarrow[-HO\cdot]{}$$

$$R-\overbrace{CH-CH_2-CH}^{O}-R^1$$

(Reaction Sequence 4.20)

The termination reaction proceeds through primary and secondary peroxy radicals according to Reaction (4.14), but at temperatures above 120°C these peroxy radicals also interact in a non-terminating way to give primary and secondary alkoxy radicals, Reaction (4.21) [6]. These radicals again contribute to the formation of cleavage products via Reactions (4.10) and (4.11):

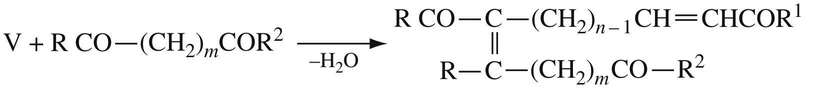
$$2ROO\cdot \rightarrow [ROOOOR] \rightarrow 2RO\cdot + O_2 \qquad \text{(Reaction 4.21)}$$

The secondary oxidation phase: At higher temperatures the viscosity of the bulk medium increases as a result of the polycondensation of the difunctional oxygenated products formed in the primary oxidation phase. Further polycondensation and polymerisation reactions of these high molecular weight intermediates form products which are no longer soluble in the hydrocarbon. The resulting precipitate is called sludge. Under thin-film oxidation conditions, as in the case of a lubricant film on a metal surface, varnish-like deposits are formed [11]. The polycondensation reactions which lead to high molecular weight intermediates (sludge precursors) can be described as follows. In the first step, aldehydes or ketones formed in the primary oxidation phase combine via an acid- or base-catalysed aldol condensation to form α,β-unsaturated aldehydes or ketones [12], Reaction sequence (4.22):

$$\mathrm{R\,CO{-}(CH_2)_{\mathit{n}}CHO + CH_3{-}COR^1} \xrightarrow[\text{(or base)}]{\text{acid}}$$

$$\mathrm{R{-}CO{-}(CH_2)_{\mathit{n}}CH{=}CHCOR^1 + H_2O}$$

V



$$\mathrm{V + R\,CO{-}(CH_2)_{\mathit{m}}COR^2} \xrightarrow[-\mathrm{H_2O}]{} \begin{array}{l}\mathrm{R\,CO{-}C{-}(CH_2)_{\mathit{n}-1}CH{=}CHCOR^1}\\ \qquad\quad \| \\ \mathrm{R{-}C{-}(CH_2)_{\mathit{m}}CO{-}R^2}\end{array}$$

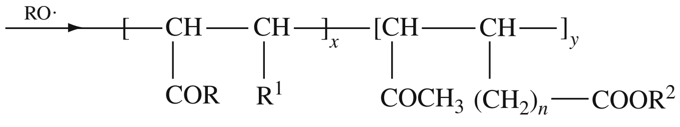
VI

(Reaction 4.22)

Further aldol condensations with species VI lead to high molecular weight but still oil-soluble polycondensation products (molecular weight about 2000 amu).

When the reaction becomes diffusion controlled as a result of the increased viscosity of the oil, alkoxy radicals can initiate polymerisation of polycondensation products. This leads to sludge and deposit formation as well as to additional oil-soluble high molecular weight products which contribute to the viscosity increase. This process can be described as co-polymerisation of two different polycondensation species in which the alkyl groups R, R^1 and R^2 could represent oxo- or hydroxy-functionalised long hydrocarbon chains Reaction (4.23):

$$x\mathrm{R{-}CO{-}CH{=}CH{-}R^1} + y\mathrm{CH_3CO{-}CH{=}CH{-}(CH_2)_{\mathit{n}}COOR^2}$$



$$\xrightarrow{\mathrm{RO\cdot}} \Big[\underset{\mathrm{COR}}{\mathrm{CH}}{-}\underset{\mathrm{R^1}}{\mathrm{CH}}\Big]_x{-}\Big[\underset{\mathrm{COCH_3}}{\mathrm{CH}}{-}\underset{\mathrm{(CH_2)_{\mathit{n}}{-}COOR^2}}{\mathrm{CH}}\Big]_y$$

(Reaction 4.23)

Condensation polymerisations are accelerated in the presence of metals such as iron [13], but lead suppresses polycondensation.

Under high-temperature conditions there is always the possibility of thermal cleavage of a hydrocarbon chain, especially when the availability of oxygen is limited by diffusion, Reaction sequence (4.24):

$$R(CH_2)_6R \rightarrow 2[CH_2CH_2{-}CH_2\cdot] \rightarrow 2RCH_2CH{=}CH_2 + H_2$$
(Reaction Sequence 4.24)

Reaction (4.24) leads to unsaturated molecules with lower molecular weight and higher volatility. The model for high-temperature oxidation is described by Fig. 4.2 [9, 10, 14, 15]:

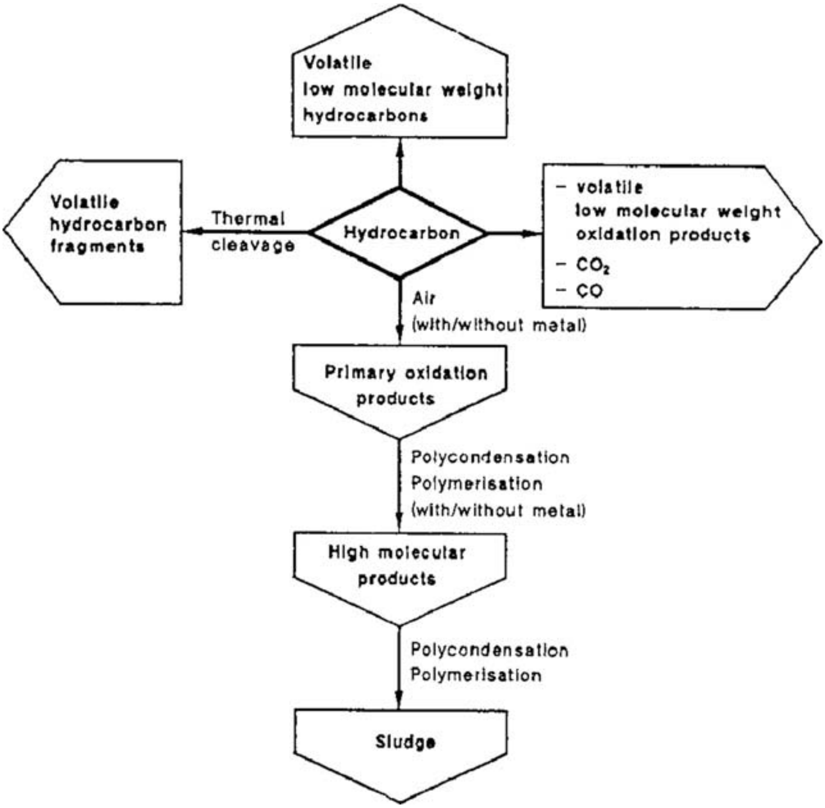


Fig. 4.2 Model of lubricant degradation under high-temperature conditions

4.2.3 Metal-Catalysed Autoxidation of Hydrocarbons

Decomposition of an alkyl hydroperoxide molecule occurs at temperatures of ~150°C. Transition metal ions with two valence states such as $Fe^{2+/3+}$, $Pb^{2+/4+}$ and $Cu^{1+/2+}$ reduce the activation energy of this decomposition process. These ions must be present as metal soaps, otherwise they are not catalytically active [16]. Hence the homolytic hydroperoxide decomposition is accelerated at ambient temperatures by small concentrations, 0.1–50 ppm, of these metals, Reactions (4.25) and (4.26), which can be summarised as Reaction sequence (4.27):

$$ROOH + M^{n+} \rightarrow RO\cdot + M^{(n+1)+} + OH^-$$ (Reaction 4.25)

$$\mathrm{ROOH} + \mathrm{M}^{(n+l)+} \rightarrow \mathrm{ROO}\cdot + \mathrm{M}^{n+} + \mathrm{H}+ \qquad \text{(Reaction 4.26)}$$

$$2\mathrm{ROOH} \rightarrow \mathrm{M}^{n+}/\mathrm{M}^{(n+1)+} \rightarrow \mathrm{ROO}\cdot + \mathrm{RO}\cdot + \mathrm{H_2O} \qquad \text{(Reaction Sequence 4.27)}$$

Chain branching under the influence of a catalyst at a given temperature proceeds faster when compared with the uncatalysed reaction. The consequence is a high rate of hydroperoxide formation (and hence oxidation), as illustrated in Fig. 4.3.

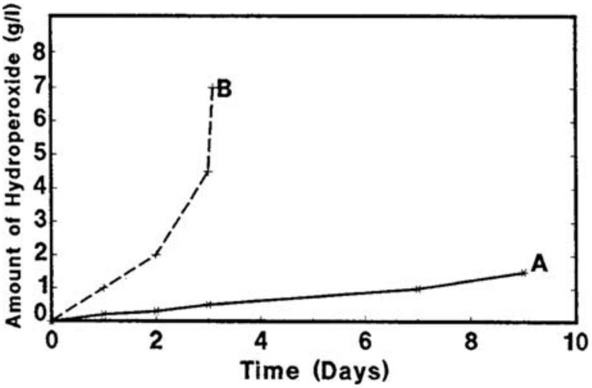


Fig. 4.3 Increase of hydroperoxide concentration under the influence of $\mathrm{Fe(OOCC_7H_{15})_3}$ in catalysis: (**A**) pure model hydrocarbon; (**B**) pure model hydrocarbon plus 500 ppm $\mathrm{Fe(OOCC_7H_{15})_3}$. Conditions: 95°C bath temperature, 300 ml oil volume; 3 l/h oxygen flow [17]

The precursor steps of soap formation, shown below with Fe as the metallic surface, arise from the attack of the metal surface by alkylperoxy radicals and alkylhydroperoxide. This process may be called ‘corrosive wear’, Reactions (4.28) and (4.29) [18, 19], where the FeO reacts further with organic acids and forms the iron soaps, Reaction (4.30):

$$\mathrm{ROO}\cdot + \mathrm{Fe} \rightarrow \mathrm{FeO} + \mathrm{RO}\cdot \qquad \text{(Reaction 4.28)}$$

$$\mathrm{ROOH} + \mathrm{Fe} \rightarrow \mathrm{FeO} + \mathrm{ROH} \qquad \text{(Reaction 4.29)}$$

$$2\mathrm{RCOOH} + \mathrm{FeO} \rightarrow \mathrm{Fe(OCOR)_2} + \mathrm{H_2O} \qquad \text{(Reaction 4.30)}$$

The catalytic activity of copper and iron can be summarised as follows [20, 21]:

- in the presence of iron, copper soaps can retard oxidation and polycondensation/polymerisation reactions from a concentration level of 200 ppm onwards, considered also in Sections 4.4.1 and 4.5.2. In iron ion-free systems, organocopper salts behave as pro-oxidants. However, from 1,000 ppm and above they can behave as effective antioxidant systems.
- iron soaps accelerate oxidation and polycondensation/polymerisation reactions with increasing concentration.

Figure 4.4 shows the retardation of oxidation by a copper salt during the oxidation of tetralin, a model hydrocarbon, in the presence of 0.5% iron stearate [22].

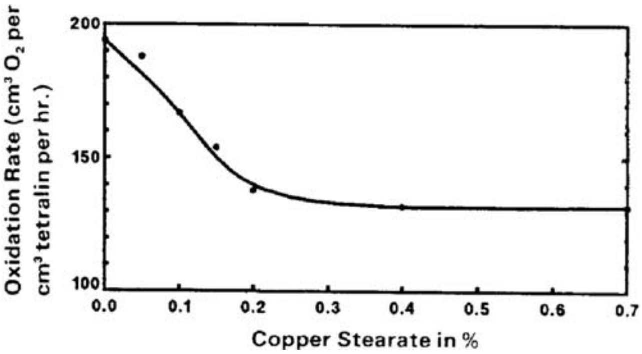


Fig. 4.4 Influence of copper stearate on the oxidation rate of the iron stearate (0.5%)-catalysed oxidation of tetralin [22]

In conclusion, the oxidation of model hydrocarbons proceeds via a radical chain mechanism and is strongly influenced by temperature and by certain transition metal ions. This results in the formation of insoluble sludge as well as a continuous increase in viscosity. The following section deals with the oxidation of base oils, which principally follows the same reaction pattern as the model hydrocarbons but is more complex due to the presence of natural inhibitors and pro-oxidants.

4.3 Oxidation Stability of Base Oils

The majority of lubricants are produced from mineral (petroleum)-based base stocks. Crude oil is distilled under atmospheric pressure to remove gasoline and distillate fuel components. The distillation residue is then vacuum distilled to remove a ‘neutral distillate’ fraction, the precursors to lubricating base stock. The neutral distillate fraction is then refined into lubricant base stock by two basic methods, either solvent refining or hydrocracking. Solvent refining, the older process, uses solvent extraction to remove fractions imparting colour, instability and reducing viscosity index. These fractions consist of aromatic compounds and heteroatoms such as nitrogen and sulphur. In hydrocracking, the neutral distillate fraction reacts with hydrogen under high pressure and temperature. Aromatic compounds are reduced to saturated cycloparaffins which can rearrange further to normal and branched paraffins. In addition, most heteroatoms are removed during hydrocracking. The result of severely hydrocracking is a lubricant base oil that is greater than 99% saturated paraffins [23]. On the other hand, significant amounts of aromatics and heteroatoms remain in solvent-refined base oils. Some of these compounds may act as natural antioxidants, others as pro-oxidants, but overall it is a well-established fact within the lubricant industry that antioxidant additive response is much greater in hydrocracked base stocks, also recognised as Group II and III base oils, than in solvent-refined Group I base oils [24–26].

4.4 Inhibition of Oxidative Degradation of Lubricants

The use of additives to control lubricant degradation requires a focus on alkyl radicals (R), alkylperoxy radicals (ROO) and hydroperoxides (ROOH). Primary alkoxy radicals (RCH_2O) and hydroxy radicals (HO) rapidly abstract hydrogen from the substrate. It is therefore very unlikely that they can be deactivated by natural or synthetic antioxidants. In practice, three additive types have proven to be successful in controlling the degradation of lubricating oils:

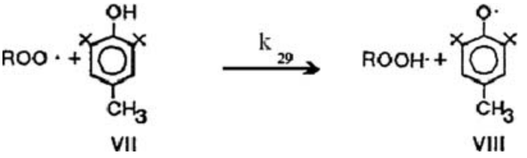
- radical scavengers,
- hydroperoxide decomposers,
- synergistic mixtures of these.

4.4.1 Radical Scavengers

The most widely used types of radical scavengers are phenolic and aminic antioxidants. The use of organometallic complexes of transition metals as antioxidants is becoming more prevalent, especially in engine oils; organomolybdenum compounds are of particular importance.

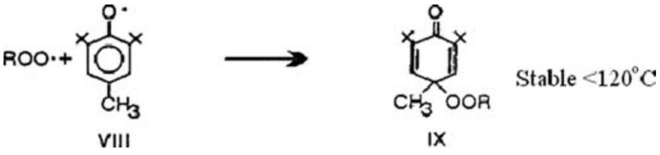
Sterically hindered phenols: Phenols substituted at the 2- and 6-positions by tertiary alkyl groups are called sterically hindered phenols, the most common substituent is the tertiary butyl group.

Reaction mechanism: Sterically hindered phenols, such as VII, compete successfully, Reaction (4.31), with the rate-determining steps of the propagation, Reaction (4.3), i.e. $k_{29} >> k_3$:



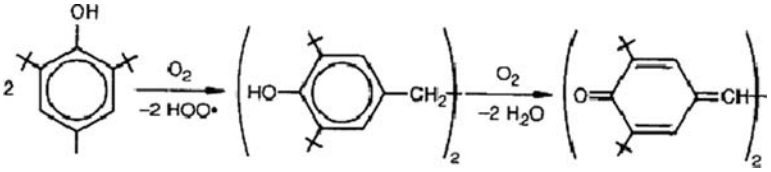
(Reaction 4.31)

The resonance-stabilised phenoxy radical, VIII, preferentially scavenges an additional peroxy radical to form a cyclohexadienone peroxide, IX, Reaction (4.32):



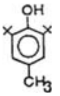
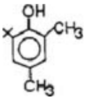
(Reaction 4.32)

An alternative reaction mechanism to Reactions (4.31) and (4.32) has been suggested concerning how sterically hindered phenols act as antioxidants for lubricants [27]. Based on the fate of 2,6-di-*tertiary*-butyl-*p*-cresol in a turbine oil used in a conventional steam turbine, it was concluded that there is a strong possibility that this phenol is consumed not through the inhibition of oxidation, Reactions (4.31) and (4.32), but via direct oxidation with oxygen, Reaction sequence (4.33):

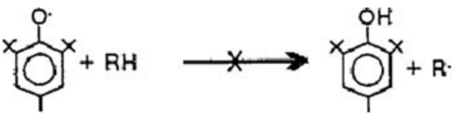


(Reaction 4.33)

Table 4.1 Influence of ortho substitution on the antioxidant activity of hindered phenols in lubricants at 0.1% and 110°C [28]

Type of Phenol	Relative Activity
	100.0
	62.5

Optimum protection of the substrate towards oxidation can be achieved when both 2- and 6-positions of the phenol are substituted with tertiary butyl groups and the 4-position is substituted with an *n*-alkyl group [28]. Replacement of a tertiary butyl group by a methyl group in the ortho position reduces the antioxidant activity considerably, Table 4.1. Steric hindrance in both ortho positions beneficially prevents hydrogen abstraction by the phenoxy radical, Reaction (4.34):

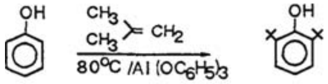
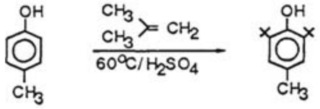
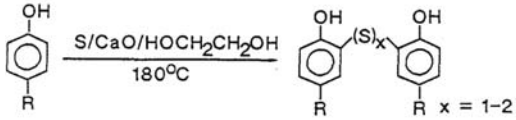
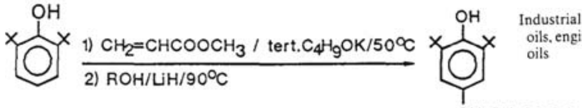
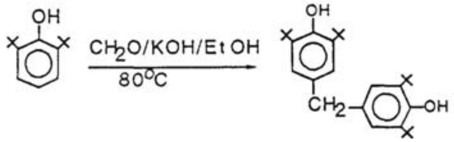


(Reaction 4.34)

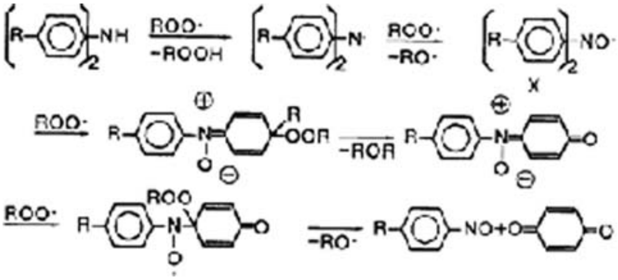
Synthesis: Global annual consumption of sterically hindered phenols for industrial lubricants and engine oils amounts to 40,000–50,000 tonnes. The major structural types which are commercially available, together with their synthetic routes, are outlined in Table 4.2, from [29–31].

Aromatic amines: Secondary aromatic amines are another important class of antioxidants used in lubricants. The principal substituents of the nitrogen atom are either two aryl or one phenyl and a naphthyl group.

Table 4.2 Major commercial phenolic antioxidants and their applications

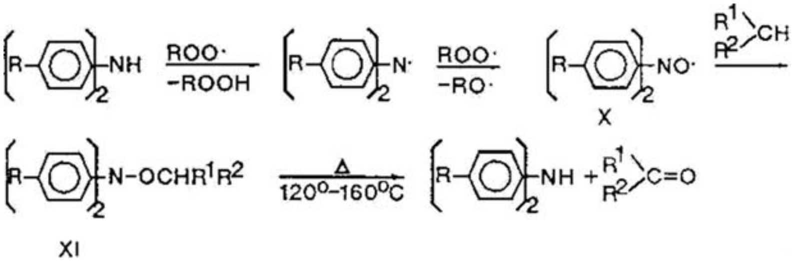
Structure and Synthesis	Major Use
	Industrial oils
	Industrial oils, greases
	Engine oils
	Industrial oils, engine oils
	Industrial oils, engine oils

Reaction mechanism: The reaction mechanism of diphenylamines is dependent on the temperature. Under low-temperature conditions, <120°C, the interaction with peroxy radicals predominates, Reaction sequence (4.35).



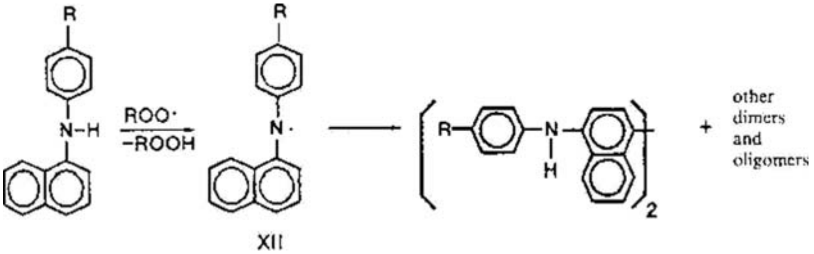
(Reaction Sequence 4.35)

According to Reaction sequence (4.35), one diphenylamine molecule eliminates four peroxy radicals and, by definition, the stoichiometric factor is 4. For a sterically hindered monophenol, this factor is 2. Hence diphenylamines perform better as peroxy radical scavengers than do monophenols at temperatures <120°C. Under high-temperature conditions, >120°C, e.g. engine oils, an extended stabilisation mechanism in the form of a catalytic cycle has been suggested, Reaction sequence (4.36) [32, 33]:



(Reaction Sequence 4.36)

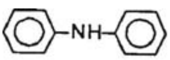
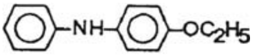
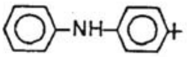
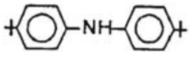
It has been demonstrated that the nitroxyl radical, X, reacts with a secondary alkyl radical to form XI which, under high-temperature conditions (>120°C), regenerates the original diphenylamine molecule, Reaction (4.36). In essence, this group of stabilisers acts catalytically by scavenging alternately peroxy (ROO·) and alkyl radicals (R·). As stated earlier, sterically hindered phenols deactivate only two peroxy radicals per phenol molecule. Hence, under high-temperature conditions, aromatic amines are far superior to their phenolic counterparts. As shown in Table 4.3, the stoichiometric factor of the diphenylamines depends on the substituents in the para position [33]. The efficacy of the diphenylamine antioxidant is improved by alkylating the para positions. The stabilisation mechanism for phenyl-α-naphthylamines, Reaction sequence (4.37) [34], is described as follows:



(Reaction sequence 4.37)

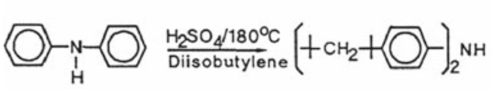
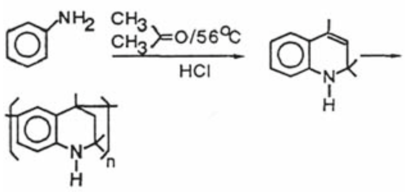
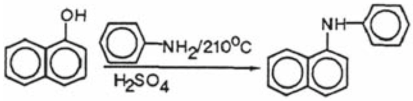
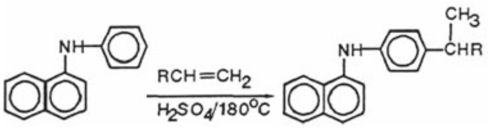
In contrast to the diphenylamine derivatives, transformation of the nitrogen radical (XII) to a nitroxyl radical, N–O·, has not been observed. Due to the longer lifetime of the nitrogen-centred radical (XII) by resonance stabilisation, dimerisation and oligomerisation take place whilst maintaining the –NH– function. Indications have been found that the products of Reaction (4.37) may result from direct reaction of phenyl-α-naphthylamine with oxygen [27, 35].

Table 4.3 Stoichiometric factors of different secondary aromatic amines, (2×10^{-5}mol l^{-1}) in a paraffinic oil at 130°C

Compound	Stoichiometric Factor
	41
	36
	53
	52

Synthesis: The present annual consumption of this class in the lubricant industry is believed to be about 50,000–60,000 tonnes. Representatives of this class of compounds together with their syntheses are outlined in Table 4.4 [36].

Table 4.4 Major commercial aminic antioxidants and their applications

Structure and Synthesis	Major Use
	Industrial lubricants, engine oils, aviation oils, automatic transmission fluids, greases
	Greases
	Industrial lubricants, greases
	Industrial lubricants, engine oils, aviation oils, greases

Organometallic complexes of transition metals: Transition metals are characterised by their ability to exist in more than one oxidation state, which gives them catalytic activity in many chemical and biological processes. For the autoxidation and stabilisation of hydrocarbons such as mineral oil, it is proposed that transition metals can either catalyze or inhibit autoxidation by the following set of reactions [37]. In Reaction sequences (4.38) and (4.39), transition metals can catalyze oxidation by complexing and then decomposing hydroperoxides to form chain-propagating alkoxy and peroxy radicals, respectively:

$$M^{n+} + ROOH \rightleftharpoons (ROOHM)^{n+}$$
$$(ROOHM)^{n+} \rightleftharpoons RO\cdot + M^{(n+1)+} + OH^-$$

(Reaction Sequence 4.38)

$$M^{(n+1)+} + ROOH \rightleftharpoons (ROOHM)^{(n+1)+}$$
$$(ROOHM)^{(n+1)+} \rightleftharpoons RO_2\cdot + M^{n+} + H^+$$

(Reaction Sequence 4.39)

On the other hand, transition metals are also capable of oxidising peroxy radicals and reducing alkyl radicals to inert products, as in Reactions (4.40) and (4.41):

$$RO_2\cdot + M^{n+} \rightleftharpoons M^{(n+1)+} + \text{Inert Products}$$ (Reaction 4.40)

$$R\cdot + M^{(n+1)+} \rightleftharpoons M^{n+} + \text{Inert Products}$$ (Reaction 4.41)

Thus, transition metals are capable of catalytically scavenging free radicals, as for copper in Fig. 4.5, if the copper concentration exceeds that of the hydroperoxide [38].

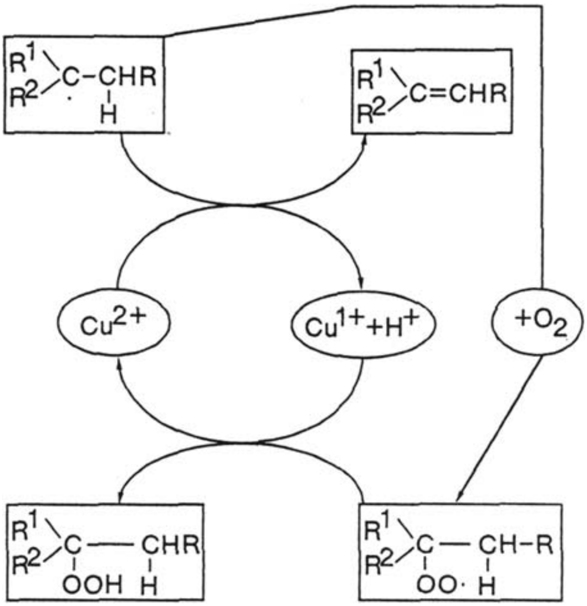
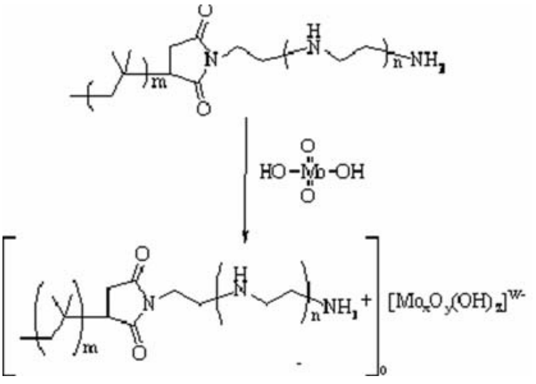


Fig. 4.5 Catalytic radical scavenging mechanisms of copper ions in engine oils

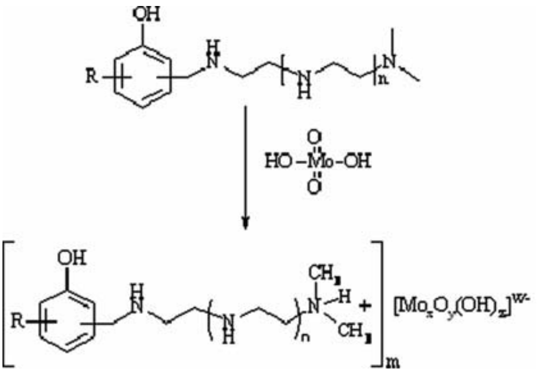
For organocopper compounds, the objective is accomplished by using copper concentrations above 100 ppm in combination with compounds that preferably complex and/or decompose hydroperoxide (hydroperoxide decomposers are discussed in the next section). Examples of compounds that preferably complex and/or decompose hydroperoxide are primary, secondary and tertiary amines, dialkylselenides, trialkyl phosphines, trialkyl phosphites [37] and zinc dialkyldithiophosphates and thiadiazoles [39].

Although the antioxidant mechanism of organocopper is better understood, it is organomolybdenum that has found more significant use in the stabilisation of lubricants, particularly in engine oils. It has been reported that one in four passenger cars and trucks in the United States contains a particular type of molybdenum compound [40]. Unpublished analysis collected by the authors confirms that a significant number of the major engine oil brands meeting API SL specifications contain 50–100 ppm of molybdenum. Surveying the patent literature indicates that the success of molybdenum as an antioxidant is due to its synergy with other antioxidants, in particular aminic antioxidants such as alkylated diphenylamines. The rest of this section is dedicated to a patent survey on organomolybdenum compounds and their use in lubricating compositions.

Ammonium oxymolybdenum complexes with amines: These complexes are prepared by the acid/base reaction of an acidic molybdenum source such as molybdenum trioxide, molybdic acid, ammonium molybdate [41] and ammonium thiomolybdates with oil-soluble amines [42]. The preferred aminic compounds are lubricant additives known as dispersants, examples being succinimides and Mannich-type bases, as in Reactions (4.42) and (4.43) [41]:



(Reaction 4.42)



(Reaction 4.43)

In lubricating compositions, these compounds show excellent antioxidant synergy with aromatic amines such as alkylated diphenylamines [43] and sulphur compounds such as metal dihydrocarbyl dithiophosphate, a metal dithiocarbamate, sulphurised olefins, alkyl and aryl sulphides, alkyl and aryl polysulphides, sulphurised carboxylic acid esters, sulphurised alkylphenols, reaction product of an olefin and sulphurised alkylphenol, and phosphosulphurised terpenes or mixtures thereof [43].

Molybdenum dialkyldithiocarbamates: Molybdenum dialkyldithiocarbamates are multifunctional lubricant additives as anti-wear, anti-friction and antioxidants. Molybdenum dialkyldithiocarbamates are also multifunctional antioxidants due to the hydroperoxide decomposing ability of dialkyldithiocarbamates, see Section 4.4.2, and the radical scavenging capacity of molybdenum. The best established structure for molybdenum dialkyldithiocarbamates is a six-coordinate complex of a dinuclear molybdenum centre with each molybdenum bonded to terminal oxygen or sulphur atoms, two bridging oxygen or sulphur atoms and one dialkyldithiocarbamate ligand, Fig. 4.6 [44]:

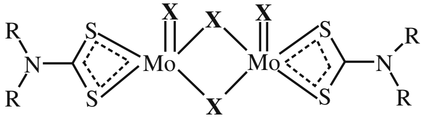


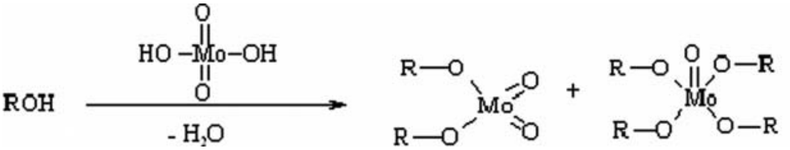
Fig. 4.6 Structure of dinuclear molybdenum dialkyldithiocarbamate, where X are oxygen and sulphur atoms

The preparation typically involves a condensation reaction of acidic molybdenum sources such as molybdenum trioxide, molybdic acid and ammonium molybdate with dialkylammonium dialkyldithiocarbamate salts formed in situ by reaction of carbon disulphide and dialkylamine [45]. The extent of sulphurisation of the molybdenum core can be increased by the introduction of sulphurising agents such as sodiumhydrosulphide [46]. Patent literature reports that the greatest antioxidant effect of molybdenum dialkyldithiocarbamates is seen when combined with aminic and phenolic antioxidants [47].

Together with dinuclear molybdenum dialkyldithiocarbamates, trinuclear dialkyldithiocarbamates have recently been introduced for lubricant applications, specifically for use in engine oils [48]. These molecules are based upon $[Mo_3S_4]^{4+}$ and $[Mo_3S_7]^{4+}$ cores complexed by four dialkyldithiocarbamate ligands. It has been reported that these products decompose hydroperoxides more effectively than do dinuclear molybdenum dialkyldithiocarbamates. The patent literature discloses trinuclear molybdenum dialkyldithiocarbamates that are most effective as antioxidants when combined with radical scavengers such as organocopper compounds and diphenylamines [49].

Molybdenum carboxylates: These complexes, also known as 'molybdenyl carboxylates', are derived from such carboxylic acids as naphthenic, 2-ethylhexanoic and octanoic acids. The basic structure of the molybdenyl group is a mononuclear dioxo-metal centre, $(MoO_2)^{2+}$. They are prepared by condensation reactions of the carboxylic acid and molybdenum sources such as molybdic acid and ammonium molybdate in the absence or presence of organic amine catalyst [50], also by using molybdenyl bis-acetylacetonate [51]. The patent literature states that molybdenum carboxylates are exceptional antioxidant synergists with diaryl amines [52] and with combinations of diaryl amines and sulphurised hindered phenols and/or sulphurised olefins [53].

Molybdate esters: These compounds are prepared by reaction of alkanols and molybdenum sources such as ammonium molybdate and molybdenum oxides, and are believed to form mononuclear mono- and dioxo- structures, as in Reaction (4.44) [54, 55]. These preparations are condensation reactions and require removal of water to drive the reaction to completion. Molybdate esters, like molybdenum carboxylates, show synergistic effects with diaryl amines [52] and with combinations of diaryl amines and sulphurised hindered phenols and/or sulphurised olefins [53].

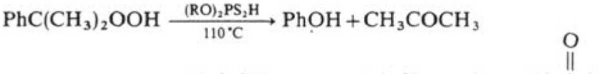


(Reaction 4.44)

4.4.2 Hydroperoxide Decomposers

These compounds convert hydroperoxides into non-radical products, thus preventing the chain propagation reaction. Traditionally, organosulphur and organophosphorus additives have been used for this purpose.

Organosulphur compounds – Reaction mechanism of organosulphur compounds: The most important reaction mechanism to eliminate hydroperoxides is their acid-catalysed decomposition. The catalysts are protic (RSO$_2$H) or Lewis (SO$_2$) acids [56, 57], Reaction sequences (4.45) and (4.46):



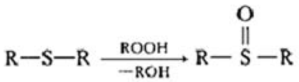
$$\mathrm{PhC(CH_3)_2OOH \xrightarrow[110\,^{\circ}C]{(RO)_2PS_2H} PhOH + CH_3COCH_3 + PhC(CH_3)_2OH + PhC(CH_3){=}CH_2 + Ph\overset{\overset{O}{\|}}{C}CH_3}$$

(Reaction Sequence 4.45)

$$\mathrm{[(RO)_2PS_2]_6Zn_4O \rightleftharpoons 3[(RO)_2PS_2]_2Zn + ZnO}$$

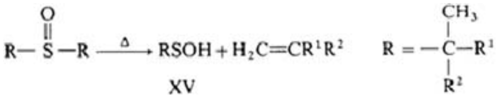
(Reaction Sequences 4.46)

Organosulphur compounds are the main source for the formation of the acid catalyst. Compounds such as XIII react with hydroperoxides to yield sulphoxides, XIV, as key intermediates for the stabilisation of the lubricant [58–60], (Reaction 4.47):



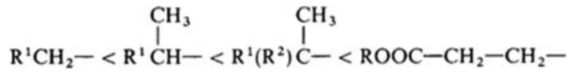
$$\underset{\text{XIII}}{R{-}S{-}R} \xrightarrow[-ROH]{ROOH} \underset{\text{XIV}}{R{-}\overset{O}{\overset{\|}{S}}{-}R} \qquad \text{(Reaction 4.47)}$$

Thermolytic cleavage of species like XIV form sulphenic acid, XV, Reaction (4.48):



$$R{-}\overset{O}{\overset{\|}{S}}{-}R \xrightarrow{\Delta} \underset{\text{XV}}{RSOH} + H_2C{=}CR^1R^2 \qquad R = {-}\overset{CH_3}{\underset{R^2}{C}}{-}R^1 \qquad \text{(Reaction 4.48)}$$

The influence of the structure of the alkyl group, R, on the rate of cleavage in Reaction (4.48) has been correlated with the following order of increasing reactivity:



$$R^1CH_2{-} < R^1\overset{CH_3}{C}H{-} < R^1(R^2)\overset{CH_3}{C}{-} < ROOC{-}CH_2{-}CH_2{-}$$

Further reaction of acid XV with hydroperoxide leads to the formation of sulphinic acid, Reaction (4.49). Sulphinic acids are the most important acid catalysts for ionic decompositions below 100°C. At higher temperatures, SO_2 resulting from Reaction (4.50) is a most efficient catalyst [59, 60]:

$$R{-}SOH + ROOH \rightarrow RSO_2H + ROH \qquad \text{(Reaction 4.49)}$$

$$R{-}SO_2H \xrightarrow{\Delta} R{-}H + SO_2 \qquad \text{(Reaction 4.50)}$$

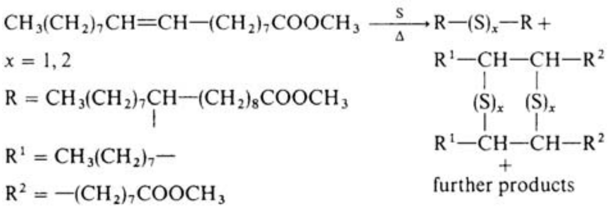
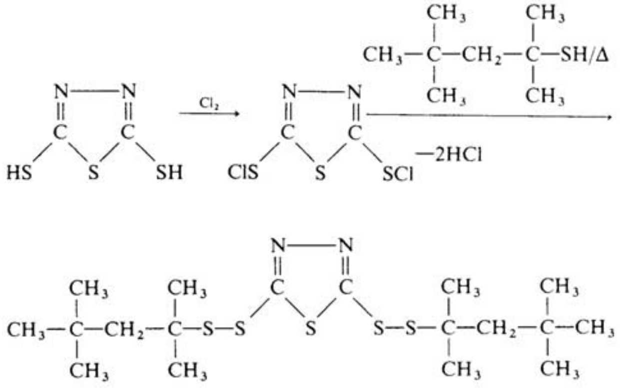
Dialkyl disuphides (R−S−S−R) follow the same reaction pattern, finally forming a thiosulphurous acid, $RS{-}SO_2H$, which under higher temperature and in the presence of hydroperoxides is cleaved to give SO_2 and a sulphenic acid, RSOH. An additional stabilisation mechanism is peroxy radical scavenging by sulphacids, RSO_xH, Reaction (4.51):

$$RSO_xH \xrightarrow{ROO\cdot} RSO_x\cdot + ROOH \qquad x = 1,2,3 \qquad \text{(Reaction 4.51)}$$

These stabilisation mechanisms work if a high molar $ROOR/R{-}S_x{-}R$ ratio exists. At low molar ratios, sulphides (R−S−R) and disulphides (R−S−S−R) show a certain pro-oxidant effect. This behaviour is one of the reasons why the organosulphur compounds only contribute positively to oxidation stability after the phenolic antioxidants have been depleted and the molar ratio of $ROOH/R{-}(S)_x{-}R$ is high.

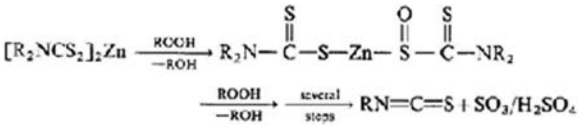
Synthesis: The major types of organosulphur compounds together with their synthetic routes are shown in Table 4.5 [61, 62].

Table 4.5 Major types of organosulphur compounds and their synthesis

Structure and synthesis	Major use
	Industrial oils, engine oils
	Industrial oils Engine oils

Zinc dialkyldithiocarbamates: These compounds are mainly used as antioxidants although, like the ZnDTPs, they also have extreme pressure activity.

Reaction mechanism: The formation of sulphur acids, which serve as the catalyst for ionic hydroperoxide decomposition, arises through the oxidation of zinc dithiocarbamates by hydroperoxides, Reaction sequence (4.52) [63]:

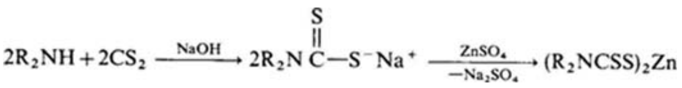


$$[R_2NCS_2]_2Zn \xrightarrow[-ROH]{ROOH} R_2N-\overset{S}{\overset{\|}{C}}-S-Zn-\overset{O}{\overset{\|}{S}}-\overset{S}{\overset{\|}{C}}-NR_2 \xrightarrow[-ROH]{ROOH} \xrightarrow[\text{steps}]{\text{several}} RN{=}C{=}S + SO_3/H_2SO_4$$

(Reaction Sequence 4.52)

In addition, zinc dithiocarbamates also act as radical scavengers, whereas in the literature, the main emphasis is generally put on their capability to destroy hydroperoxides. Their areas of application are grease and engine oils.

Synthesis The synthesis of zinc dialkyldithiocarbamates is as in Reaction sequence (4.53) [64]:



$$2R_2NH + 2CS_2 \xrightarrow{NaOH} 2R_2N\overset{S}{\overset{\|}{C}}-S^-Na^+ \xrightarrow[-Na_2SO_4]{ZnSO_4} (R_2NCSS)_2Zn$$

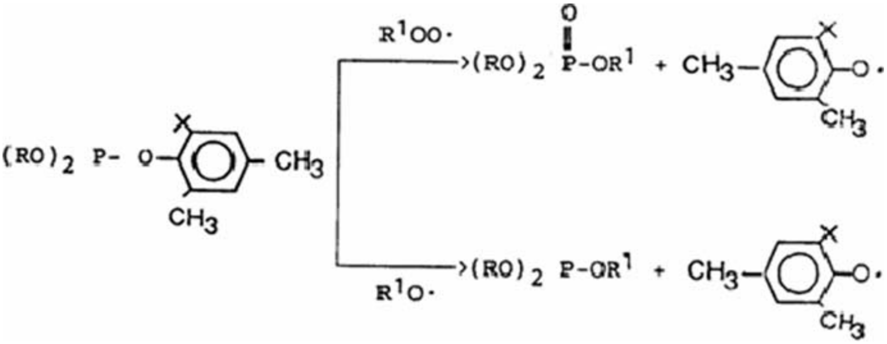
(Reaction Sequence 4.53)

Organophosphorus compounds: Phosphites are the main organophosphorus compounds used to control oxidative degradation of lubricants. They eliminate hydroperoxides, peroxy and alkoxy radicals, retard the darkening of lubricants over time and also limit photodegradation. These performance characteristics may be of importance for polyalphaolefins, hydrocracked or severely hydrotreated base stocks and white oils.

Reaction mechanism: The major non-radical mode of action is the reduction of hydroperoxides, especially under high-temperature conditions, Reaction (4.54):

$$(RO)_3P + R^1OOH \rightarrow (RO)_3P{=}O + R^1OH \qquad \text{(Reaction 4.54)}$$

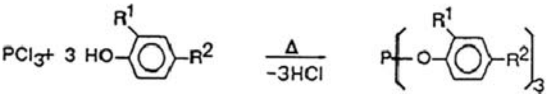
Phosphites with substituted phenoxy groups also behave as peroxy and alkoxy radical scavengers forming relatively stable phenoxy radicals, which again eliminate peroxy radicals, Reaction (4.55):



(Reaction 4.55)

When comparing the importance of these three stabilisation steps for lubricants, there appears to be a preference for the decomposition of hydroperoxide, Reaction (4.54) [65].

Syntheses The following route, Reaction (4.56), is widely used [66]:



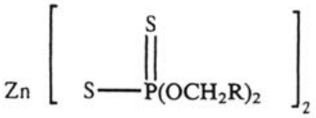
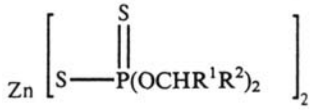
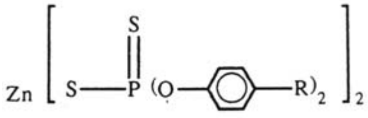
(Reaction 4.56)

4.4.3 Multifunctional Additives

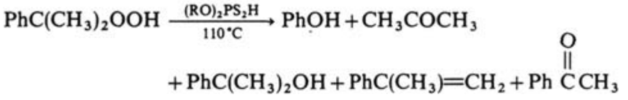
Zinc dithiophosphates: The dominating position of ZnDTPs as additives for lubricating oils is due to their multifunctional performance. Not only do they act as antioxidants, but they also improve the wear inhibition of the lubricant and protect metals against corrosion. ZnDTPs are mainly used to formulate anti-wear hydraulic fluids and engine oils.

Reaction mechanism: The performance of ZnDTPs is strongly influenced by the type of alcohols used for their synthesis. Table 4.6 gives an overview of the variance of performance with the type of alcohol.

Table 4.6 Structure–activity dependence of ZnDTPs

	Function		Property	
Structure	Oxidative inhibition	Wear protection	Thermal stability	Hydrolytic stability
Primary ZnDTP				
 $Zn\left[S{-}\overset{S}{\overset{\|}{P}}(OCH_2R)_2\right]_2$	Satisfactory	Satisfactory	Good	Satisfactory
Secondary ZnDTP				
 $Zn\left[S{-}\overset{S}{\overset{\|}{P}}(OCHR^1R^2)_2\right]_2$	Good	Good	Moderate	Good
Aryl ZnDTP				
	Moderate	Bad	Very good	Bad

The performance of ZnDTP as an antioxidant is a complex interaction pattern involving hydroperoxides and peroxy radicals. The performance matrix is additionally influenced by other additives present in industrial or engine oil formations. In a model system comprising cumene hydroperoxide and diverse ZnDTPs, it was demonstrated that the antioxidant mechanism proceeds by an acid-catalysed ionic decomposition of the hydroperoxide. The catalyst species is *O,O′*-dialkyl-hydrogendithiophosphate, $(RO)_2PS_2H$, derived from the ZnDTP, Reaction (4.57):



$$PhC(CH_3)_2OOH \xrightarrow[110°C]{(RO)_2PS_2H} PhOH + CH_3COCH_3 + PhC(CH_3)_2OH + PhC(CH_3){=}CH_2 + Ph\overset{O}{\overset{\|}{C}}CH_3$$

(Reaction 4.57)

Whilst the first four products are the result of an acid-catalysed cationic chain reaction, the acetophenone is formed by a free radical mechanism. There are two inter-related mechanisms for the formation of the acid catalyst. In the first, a rapid, initial reaction of ZnDTP and hydroperoxide forms a basic ZnDTP and a disulphide (XVI), Reaction (4.58):

$$4[(RO)_2PS_2]_2Zn + R^1OOH \xrightarrow{-R^1OH} [(RO)_2PS_2]_6Zn_40 + \underset{\text{XVI}}{[(RO)_2PS_2]_2}$$

(Reaction 4.58)

An induction period follows where the rate of decomposition of the hydroperoxide is slow; in this reaction phase, the basic ZnDTP dissociates to form ZnDTP and ZnO, Reaction (4.59):

$$[(RO)_2PS_2]_6Zn_4O \rightleftharpoons 3[(RO)_2PS_2]_2Zn + ZnO$$ (Reaction 4.59)

The ZnDTP then reacts with hydroperoxide to form additional disulphide (XVI), via the dithiophosphoryl radical (XVII), Reaction sequence (4.60):

$$[(RO)_2PS_2]_2Zn + R^1OOH \xrightarrow[-R^1O\cdot]{} [(RO)_2PS_2]ZnOH + \underset{\text{XVII}}{(RO)_2PS_2\cdot}$$

$$\underset{\text{XVII}}{2(RO)_2PS_2\cdot} \longrightarrow \underset{\text{XVI}}{[(RO)_2PS_2]_2}$$

(Reaction Sequence 4.60)

The kinetics of the reaction results in a final rapid decomposition of the hydroperoxide, provided that the concentration of the basic ZnDTP is low. Under these conditions the sulphur radical is unable to dimerise, instead it reacts with hydroperoxide leading to the catalytically active acid, Reaction (4.61):

$$(RO)_2PS_2\cdot + R^1OOH \xrightarrow{-ROO\cdot} (RO)_2PS_2H$$ (Reaction 4.61)

The second source of this acid arises when the ZnDTP concentration falls below a critical level. Then traces of water interact with ZnDTP forming the acid catalyst, Reaction (4.62):

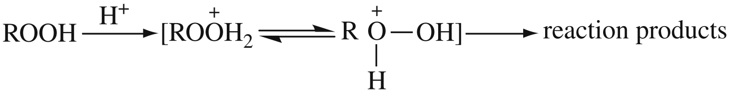
$$[(RO)_2PS_2]_2Zn + H_2O \rightarrow [(RO)_2PS_2]ZnOH + (RO)_2PS_2H$$ (Reaction 4.62)

At temperatures above 125°C the disulphide, XVI, could be an additional source of the acid catalyst via Reaction (4.63) followed by Reaction (4.61) [69]:

$$\underset{\text{XVI}}{[(RO)_2PS_2]_2} \longrightarrow \underset{\text{XVII}}{2(RO)_2PS_2\cdot}$$

(Reaction 4.63)

A general scheme for the decomposition of hydroperoxides may be written as follows, Reaction (4.64):



$$ROOH \xrightarrow{H^+} [RO\overset{+}{O}H_2 \rightleftharpoons R\underset{H}{\overset{+}{O}}-OH] \longrightarrow \text{reaction products}$$

(Reaction 4.64)

The type of reaction products formed is in accordance with Reactions (4.45) and (4.50). ZnDTP may also interact with peroxy radicals according to Reaction (4.65) [70]:

$$[(RO)_2PS_2]_2Zn \xrightarrow{ROO\cdot} RO_2^- + (RO)_2PS_2Zn^+ + \underset{\text{XVII}}{(RO)_2PS_2^{\cdot}} \qquad \text{(Reaction 4.65)}$$

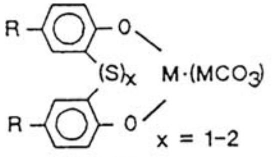
The XVII radical may react again with hydroperoxide, Reaction (4.66), thereby generating the acid $(RO)_2PS_2H$, which is a better inhibitor than the ZnDTP.

Synthesis: About 150,000–160,000 tonnes per year are produced in the western world by Reaction sequence (4.66):

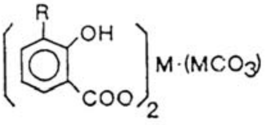
$$\begin{aligned} &P_2S_5 + 4ROH \rightarrow 2(RO)_2PS_2H + H_2S \\ &2(RO)_2PS_2H + ZnO \rightarrow [(RO)_2PS_2]_2Zn + H_2O \end{aligned} \qquad \text{(Reaction Sequence 4.66)}$$

Primary and secondary aliphatic alcohols with chain lengths from C_3 to C_{12} and alkylated phenols are used. Aryl ZnDTPs are now less important than alkyl ZnDTPs. Very often mixtures of low, $<C_5$, and high molecular weight alcohols, $>C_5$, are used for the synthesis. If only one type of alcohol is used, R should contain at least five carbon atoms.

Overbased phenates and salicylates: Both phenates and salicylates of magnesium or calcium behave as antioxidants at high temperatures. The antioxidant activity may be related to hydroperoxide decomposition by the sulphur in structure XVIII and peroxy radical scavenging by the OH group in structure XIX [71]. Addition of MCO_3 to phenates and salicylates leads to the corresponding overbased products, which also act as acid scavengers.

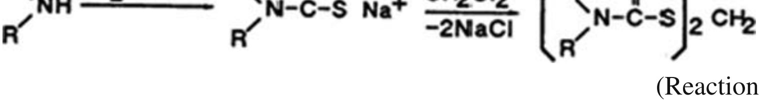


XVIII M = Ca, Mg

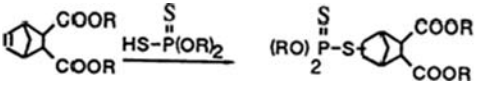


XIX M = Ca, Mg

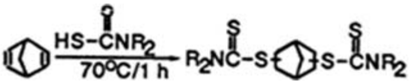
Sulphur/nitrogen and sulphur/phosphorus compounds: Other multifunctional sulphur/nitrogen, sulphur/phosphorus-based additives have antioxidant and antiwear properties. These additives react with peroxy radicals and hydroperoxides, thus stabilising industrial lubricants and engine oils. Syntheses and generalised chemical structures are as in Reactions (4.67–4.69) [64, 72, 73]:



(Reaction 4.67)



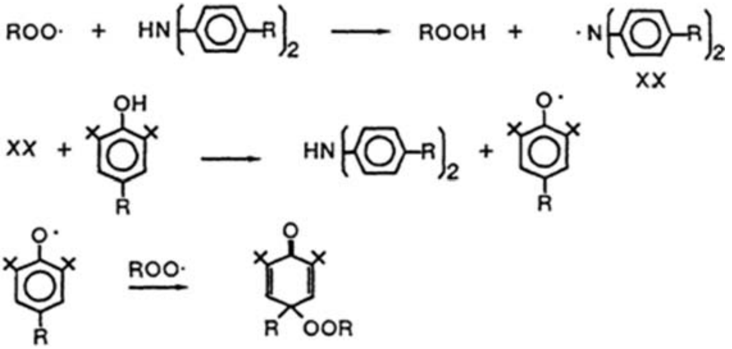
(Reaction 4.68)



(Reaction 4.69)

4.4.4 Synergism Between Antioxidants

The effectiveness of one class of antioxidant may be enhanced by combining it with another type of stabiliser. Hence, combining two different peroxy radical scavengers in a lubricant gives improved oxidation stability compared with either alone. This form of additive response is called synergism or, more specifically, homosynergism because they operate by the same stabilisation mechanism. The mechanism of this synergism is outlined as Reaction sequence (4.70) [74]:



(Reaction Sequence 4.70)

The aminic antioxidant reacts faster than the phenolic antioxidant with the peroxy radical. The less efficient sterically hindered phenol then regenerates the more effective aminic antioxidant. An additional interesting example of how the oxidation stability of a lubricant can be optimised by using a synergistic combination of an aminic antioxidant and an organosulphur hydroperoxide decomposer, instead of the alkylated diphenylamine alone, is outlined in Table 4.7. This type of interaction is called heterosynergism because two different stabiliser mechanisms are involved. This occurs due to the organosulphur compound decomposing the majority of hydroperoxides. Fewer radicals which initiate chain reactions are formed, and therefore less aminic antioxidant is consumed by the peroxy radical scavenging process.

Table 4.7 Oxidation stability of a lubricant stabilised with a synergistic antioxidant combination

Test fluid			
Alkylated diphenylamine	0.25%	–	0.20%
$S(CH_2CH_2 \cdot COOR)_2$	–	0.25%	0.05%
Rust inhibitor	0.05%	0.05%	0.05%
Base stock	balance	balance	balance
*Oxidation stability**			
Time (h) to TAN = 2	2000	200	3300
Sludge (mg)	172	>5000	89

*TOST, ASTM D943 (95°C, H_2O, Fe and Cu catalyst)
Base oil characteristics ISO VG32, C_A(aromatic carbon) = 6.5%, S = 0.54% TAN units in mg KOH/g oil

4.5 Application of Antioxidants

4.5.1 Industrial Lubricants

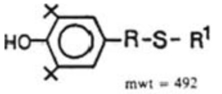
Industrial lubricants have to prevent damage to the machinery which arises from friction between moving parts in service. Oxidation stability is one of the key requirements of the lubricant because the oxidation degradation products, e.g. peroxy radicals, hydroperoxides and organic acids as well as sludge and deposits, are detrimental to the equipment. The important role of antioxidants, to protect the various types of base oil under different operation conditions, is outlined in the following sections.

Turbine oils: The ratio between the power output of turbines and oil volume has increased considerably over the years. Consequently, operating temperatures have increased from 100 to 160°C [75]. Legislated emission regulations and growth in electrical power demand are boosting gas turbines as the most important cogeneration unit. The combined generation of electric power and useful thermal energy, using the normally wasted gas turbine exhaust heat to drive a steam turbine, is called cogeneration or combined cycle gas turbine, CCGT. The conditions under which the lubricant has to function in a gas turbine are even more demanding from thermo-oxidative and volatility considerations. General Electric Frame 7 gas turbine oil specification, GEK 32568, excludes the use of 2,6-di-*tertiary*-butyl-*p*-cresol, BHT, owing to its volatility under these conditions. With the introduction of cogeneration, the need for a turbine lubricant which simultaneously meets the specifications of both steam and gas turbines will grow. Thus, protecting the lubricant against high-temperature degradation by selecting more thermally stable and less volatile antioxidants has become important.

Antioxidant technology: The more stringent requirements in terms of extended lifetime and reduced sludge can be met with new antioxidants. Table 4.8 compares such a new stabiliser in the TOST test against the traditionally used 2,6-di-*tertiary*-butyl-*p*-cresol, BHT, in a hydrotreated, HT, and solvent neutral, SN, oil. The antioxidant, in combination with the corrosion inhibitor, represents the most basic type of turbine oil blend. These results can be interpreted as follows:

- the sulphur-containing, low-volatility antioxidant outperforms BHT as a result of autosynergism between the phenol and the thioether groups incorporated into the same molecule,
- the oxidation stabilities of the test fluids formulated with hydrotreated base stocks are better than the other two. In the solvent neutral base stock, antioxidant efficacy is reduced because of interactions with certain polar base stock components, especially aromatics and nitrogen-containing compounds. In addition, naturally present pro-oxidants reduce base stock stability further.

Table 4.8 Comparison of oxidation stability of turbine oils antioxidants in a hydrotreated and solvent neutral base stock

Test Fluids	Hydrotreated, HT		Solvent Neutral, SN	
	0.25%		0.25%	
		0.25%		0.25%
Corrosion Inhibitor	0.05%	0.05%	0.05%	0.05%
Base Stock	balance	Balance	balance	balance
*Oxidation Stability**				
Time to TAN = 2	4300	2400	2200	1100
Sludge, mg**	6	39	28	47
Base Stock Characteristics				
ISO VG	32		32	
C_A (aromatic content)	Nil		6.5	
Sulphur	Nil		0.54	

*Oxidation stability by TOST (ASTM, 95°C,H_2O, Fe and Cu catalysts, 3l air/h), **By ASTM 4310

The above result, that the antioxidant response in two-stage hydroprocessed oils is clearly better than in solvent-refined base stocks, has recently been confirmed [76]. It was demonstrated that phenolic-based formulations, blended into two-stage hydroprocessed oils, gave the greatest oxidative stability when total and polynuclear aromatics were lowest. Most fully formulated turbine oils make use of the synergistic interaction between phenolic and aminic antioxidants, see Reaction (4.70). Thus, depending on the performance requirements and the base oil composition, phenol/amino ratios of 1:1 to 4:1 are used [77].

Anti-wear hydraulic fluids –Requirements: Increased severity of pump operations and the trend to more universally applicable hydraulic fluids lead to the following requirements:

- improved oxidation stability,
- reduced sludge formation (better filterability),
- higher thermal stability,
- less internal friction (energy conservation),
- good hydrolytic stability (Hagglunds–Denison specification),
- excellent filterability (new pump filterability rig test: Perez and Brenner [78]).

Two classes of lubricants have emerged which fulfil these stringent requirements:

- premium-grade ashless (ZnDTP-free) lubricants,
- premium-grade, ZnDTP-based lubricants containing calcium detergents for improved thermal and hydrolytic stability of the ZnDTP.

For less severe operations, 'normal' ashless and ZnDTP-based anti-wear hydraulic fluids (AWHF) are still used. All basic hydraulic fluid formulations generally comprise antioxidant, corrosion inhibitor and anti-wear additives. The premium grades may contain up to seven further additives depending on performance requirements. For example, where extremely low-sludge figures are required, the use of dispersant VI-improvers may be considered [79]. Addition of metal deactivators protects the metal surface and thus boosts the oxidation stability of the fluid by preventing dissolution of metal ions. Overall, high-performance fluids contain 0.9–1.2% additives to meet the relevant Hagglunds–Denison, Vickers, DIN and Cincinnati Milacron specifications.

Antioxidant technology: To indicate the oxidation and thermal stability of a variety of ZnDTP-containing and ashless anti-wear hydraulic fluids, TOST and Cincinnati Milacron data – both relevant tests for this type of fluid – have been compiled and summarised, Table 4.9, from both published [80, 81] and in-house results. The data show that oxidation resistance and thermal stability of the premium fluids, both ashless and stabilised ZnDTP, are comparable and clearly outperform the normal-grade fluids. The normal ashless grade at 0.4–0.5% additives is superior to the normal ZnDTP-based grade, especially for thermal stability, which may be due to the use of thermally unstable secondary ZnDTPs.

To boost the oxidation stability of fluids formulated with stabilised ZnDTPs, in most cases, zinc di-2-ethylhexyldithiophosphate, phenolic or aminic antioxidants are often added in combination. In a similar manner to the ashless antioxidants, the response pattern of the ZnDTPs used in these fluids is strongly influenced by the degree of raffination of the base stock [82].

Although the performance of ZnDTP-based fluids is acceptable, their environmental aspects may bring about a change to ashless technology. In this context, a major European OEM has recently replaced a ZnDTP-based, anti-wear hydraulic fluid, AWHF, in its factories by an ashless speciality fluid meeting, amongst others,

Table 4.9 Oxidation and thermal stability of various anti-wear hydraulic fluids

	Performance of fully formulated anti-wear hydraulic fluids (additive blend concentration = 0.9–1.2%)			
Tests	Ashless premium grade	Stabilised ZnDTP, $P \sim 0.035\%$	Ashless◊ normal grade	ZnDTP, normal grade, $P \sim 0.1\%$
*Oxidation stability**				
Time (h) to TAN = 2 mg/KOH/g oil	2800–3800	2500–3400	1800–2800	1500–1800
Sludge (mg)**	35–90	45–90	140–320	130–430
Thermal stability ***				
Sludge (mg/100 ml)	6–30	5–46	6–40	150–263
Cu appearance, CM colour class	1–3	1–3(10)♦	1	10–12
Steel appearance, CM colour class	1–4	1–4	2	8

*Oxidation stability by TOST (ASTM, 95°C, H_2O, Fe and Cu catalysts, 3 l air/h);
**by ASTM 4310;
***thermal stabililty by Cincinnati Milacron test procedure A:168 at 135°C;
♦ one fluid gave a rating of 10 (black) in four different fluids:
◊ additive concentration = 0.4–0.05%

the severe Brugger–Weingarten specification. Another ‘eco-based’ driving force is demonstrated by the Great Lakes initiative in the United States which will not only regulate the zinc level in ZnDTP-based hydraulic fluids but also put a question mark on the use of water-extractable phenols such as 2-*tertiary*- or 2,4-di-*tertiary*-butyl phenol. These phenols are commonly part of antioxidant mixtures used to formulate AWHFs.

The example given in Table 4.10 illustrates the outstanding oxidation resistance of a rapeseed oil-based environmentally acceptable hydraulic fluid, containing a non-water-extractable phenolic antioxidant [83]. A similar type of non-water-extractable phenolic antioxidant provided excellent oxidation stability, TOST life >10,000 h, in a food-grade hydraulic fluid based on white oil [84]. All additives and the white oil are cleared by the (US)FDA.

Air compressors – Requirements: Air compressors, the most widely used compressor, put severe oxidation stress on the oil due to the presence of:

- hot air under high pressure,
- catalytically active metal salts and oxides, e.g. Fe_2O_3,
- condensed water, generated by compression.

These demanding conditions are exacerbated by recent trends such as continuous operations beyond 8,000 h, higher air throughput and larger power output from

Table 4.10 Oxidation stability of a rapeseed oil-based hydraulic fluid

Test fluid			
Percentage additive composition	0.6%		Specification
Alkylkated diphenylamine	0.30%		
Anti-wear additive	0.30%		
Metal deactivator	0.05%		
Anti-foam, non-silicone	0.005%		
Rapeseed oil ISO VG 32	Balance	Neat	
Oxidation stability: Baader test, DIN 51 544/3, 95°C, 3 days			
TAN increase (mg KOH/g oil)	0.28	0.94	0.8 max.
Viscosity increase at 40°C	12%	75%	20% max.
Load carrying capacity			
FZG gear test, DIN 51 354: A/8.3/90, Failure Load stage	>12	9–10	10 min.
Pump performance V104-C-10-Vickers vane pump,DIN 51 389 Pt.2: 1440/min., 140 bar, 25 l/min, 150 h, 13 mm^2/s			
Oil temperature to adjust viscosity to 13 mm^2/s (°C)	63	63	.
Weight loss (mg)	14	61*	150 max

Specification proposed to VDMA for an environmentally acceptable HETG (Hydraulic Environmentally acceptable TriGlycericide): *After 72 h the test was discontinued with a vane weight loss of 48 mg, which exceeds the limit of 30 mg (after 250 h partial run test time).

smaller units. To meet this increased oxidative stress, which could lead to sludge, carbon deposits and varnish, lubricants are exposed to increasingly severe bench testing. For top-tier compressor oils, which should meet the requirements of all types of compressors (universal compressor oil), the following specifications have been outlined [85–87]:

- Wolf strip test (DIN 51392): deposit below 50 mg,
- IP 48 (DIN 5131-1): viscosity increase after 24 h below 50%,
- Rotary bomb oxidation test (ASTM 2292): induction period above 1,000 min,
- Field tests: running time greater than 8,000 h.

In the past, only ester- or PAO-based formulations could meet these performance criteria. Recently it has been demonstrated that compressor oils based on solvent-refined, hydrotreated or hydrocracked base stocks formulated with low-volatility, thermally stable antioxidants can also fulfil these targets.

Antioxidant technology: An example of a modern compressor oil which can be used for continuous operation in excess of 8,000 h is presented in Table 4.11 [88]:

Table 4.11 Analysis of used oil from a reciprocating compressor

Hours of operation	34	4800	8600
Viscosity at 40°C (cSt)	72	73	73
TAN (mg/KOH g oil)	0.70	0.72	0.84
Solids (%)	0.01	0.04	0.04

The patent describing this development discloses that a mixture of a thermally stable phenolic antioxidant and a sterically hindered phosphite was used in a hydrotreated base stock. However, the heterosynergism between the radical scavenger (phenolic antioxidant) and the hydroperoxide decomposer (phosphite) was not shown in solvent-refined base stocks. An additional benefit of this technology is energy saving, due to extremely good control of viscosity.

4.5.2 Engine Oils – Requirements

Lubricants for internal combustion engines are exposed to severe oxidative conditions, particularly in the upper part of the piston ring and the cylinder liner zone where maximum temperatures can exceed 250°C in a passenger car engine and 300°C in a heavy-duty diesel. In these areas, thin oil films, $\sim 5 \times 10^{-7}$ m, are exposed to blow-by gases during a residence time of 2–5 min. Blow-by gases are generated in the combustion chamber and contain the following major components:

- free radicals (mainly $HO\cdot$),
- HNO_3, NO and NO_2, O_2,
- partially oxidised fuel (organic acids and olefins, especially from biofuels),
- partially oxidised lubricant components,
- metallic catalysts.

High temperatures and the reactive blow-by gases lead to rapid oxidation of the thin oil film, which is initiated by hydroxyl and NO_2 radicals [89]. Undoubtedly, the rate of oxidation in the initial phase is dominated by NO_2 according to the following reaction sequence (4.71) [89, 90]:

$$RH + \cdot NO_2 \rightarrow R\cdot + HONO \rightarrow HO\cdot + \cdot NO \qquad \text{(Reaction Sequence 4.71)}$$

The nitrogen oxides also react with fuel-derived olefins in the blow-by, leading to a so-called ‘sludge precursor’. Because the piston area and the crankcase are exposed to the same lubricant, all degradation intermediates such as free radicals, nitro (RNO_2) and nitroso compounds (RNO), nitrites (RONO), nitrates ($RONO_2$), acids, ketones and oil-soluble polycondensation and polymerisation products are transferred to the sump. In addition, the blow-by gas carrying sludge precursors condenses in the crankcase oil. With extended oil change intervals and crankcase oil temperatures up to 160°C, oil thickening, sludge and deposit formation may result.

4.5.2.1 Antioxidant technology for passenger car engine oils

Zinc dithiophosphates: Under service conditions, ZnDTPs undergo various chemical transformations and after 2,000–3,000 km they cannot be detected. However, 35% of the degraded ZnDTP products containing P–O–C bonds remain after 10,000 km and the antioxidant and anti-wear performance of the lubricant is still satisfactory [91]. Thus the antioxidant acidity up to 2,000–3,000 km is dominated by ZnDTPs and is subsequently governed by products resulting from their thermal cleavage. The contribution of ZnDTPs to the antioxidancy activity may be summarised as follows:

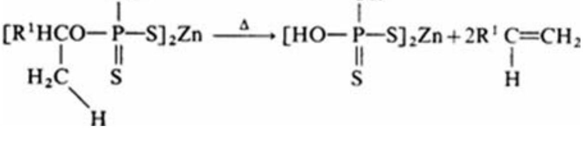
- formation of the acid catalyst $(RO)_2PSSH$ according to Reactions (4.61) and (4.62), detailed in Section 4.4.3. The intermediate disulphide $[(RO)_2PS_2]_2$ has been observed by ^{31}P NMR spectra after engine tests [92] and field tests [93]. This disulphide has a kind of 'depot' function for the acid catalyst $(RO)_2PSSH$ such that just sufficient acid is always present. If the overall available acid had been added to the oil at once, it would have been immediately neutralised by the basic detergents [94].
- catalysed ionic decomposition of hydroperoxides according to Reaction (4.64).

In addition, the following stabilisation steps can be anticipated:

- peroxy radical decomposition, Reaction (4.58),
- reduction of NO_2, Reaction (4.72):

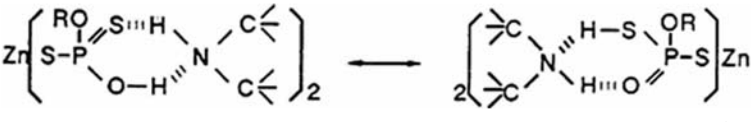
$$[(RO)_2PS_2]_2Zn + \cdot NO_2 \rightarrow NO_2^{-}(RO)_2PS_2Zn^{+} + (RO)_2PS_2\cdot \quad \text{(Reaction 4.72)}$$

Thermal cleavage of the ZnDTPs with at least one secondary alkyl group, which is completed after 2,000–3,000 km, is represented by Reaction (4.73):



(Reaction 4.73)

In the presence of dispersant in the engine oil, the following resonance-stabilised structure could be formed, Reaction (4.74):



(Reaction 4.74)

The complex formed above between the degradation products of ZnDTP and the dispersant may be the reason for the fact that the oxidation stability and also the anti-wear performance are maintained up to 10,000 km [91, 95].

A possible stabilisation step under these conditions has been suggested which may occur by the reaction of iron ions such as $Fe^{2+}/Fe^{3+}$with this complex to form the corresponding iron salts [39, 96]. Subsequent conversion to iron polyphosphates means that the iron-catalysed oxidation is suppressed.

Modern engine oils with good thermo-oxidative stability are formulated with secondary or mixed primary/secondary ZnDTPs. This is because the cleavage reaction (4.73) occurs earlier for secondary ZnDTP compared with primary ZnDTP and therefore antioxidant protection starts earlier. Sequence IIIE and VE data on API SG oil, as well as results from the field, confirm this approach [97]. Analysis of the influence of base oil composition on the oxidation stability of engine oils formulated from Group I base oils evaluated in Sequence IIID and VD engine tests [98] concluded that:

- the oxidation stability of engine oil formulated from Group I base oils is better when the base oil has a high content of sulphur and of aliphatic hydrocarbons. Olefins and nitrogen-containing organic compounds reduce this stability,
- better varnish control is achieved with engine oil formulated from Group I base oils if the base oil again has a high content of aliphatic hydrocarbons, with aromatics, olefins and nitrogen being low.

For ILSAC GF-3 engine oils in 2000, oil volatility was reduced from 20–22%, as measured by NOACK, to 15%, driving the use of lower volatility base oils, e.g. Group II in place of Group I base oils. In Europe, similar engine oil volatility limits, e.g. 13–15% NOACK volatility, adopted earlier in the 1990s drove the use of Group III and IV base oils in blends with Group I. In both instances, the resulting engine oils are inherently more oxidatively stable than earlier engine oils formulated from Group I base oils only, as evidenced by evaluation of Group I and Group II base oils treated with various ashless antioxidants, alone and in combination [99].

In addition to lower volatility requirements, modern engine oils formulated after 2004 are subject to elemental limitations on sulphur content for improved emission system compatibility, Table 4.12. These restrictions on sulphur content have essentially eliminated the use of Group I base oils in modern engine oil formulation and thereby have contributed to a great improvement in oxidative stability of modern engine oils.

Table 4.12 Lubricant specifications and sulphur content

Specification	Sulphur content (%)
ILSAC GF-4	0.5 max.
ACEA C-1	0.2 max.
ACEA C-2, C-3	0.3 max.
JASO DH-1	0.4 max.

The antioxidant performance of ZnDTP is influenced not only by the base stock composition but also by the dispersants and detergents, demonstrated by Fig. 4.7. The deleterious effect of the dispersant on the oxidation stability of the ZnDTP-containing lubricant is clearly enhanced by calcium detergents [100] and, to a larger extent, magnesium detergents [39]. In summary, the additive interaction pattern is influenced by the type of dispersant and detergent, by the base stock composition and by the concentration ratio of the additives used in a formulation [101].

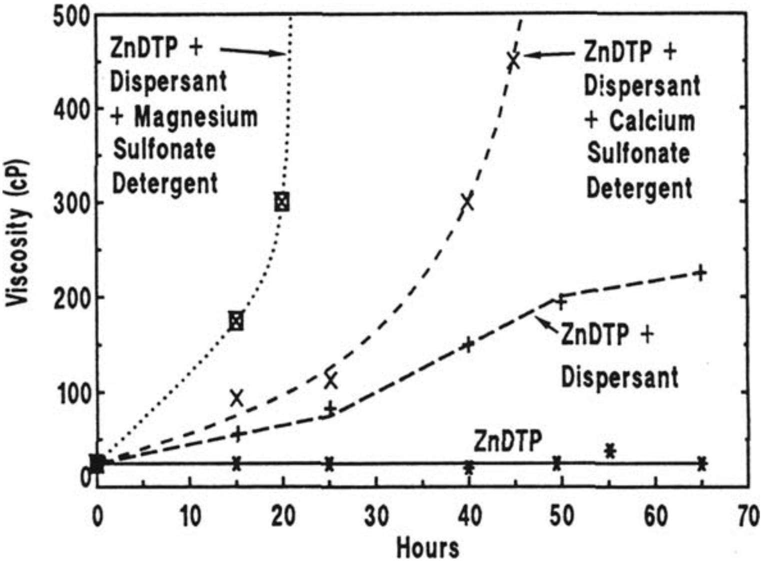


Fig. 4.7 Influence of 4.5% dispersant and 1% calcium sulphonate detergent on the antioxidant performance of a 0.1%P ZnDTP. 150SN, S = 0.3% base stock, temperature 165°C; air flow 1.7 l min^{-1}; 40 ppm Fe catalyst as ferric acetyl acetonate

Organocopper salts: During the 1980s, the successful application of organocopper salts in passenger car engine oils was made possible by the eventual selection of a concentration of copper in the range 90–120 ppm. Within this range, optimum control of oxidation and wear can be achieved [102]. The inter-relation between oxidation and wear is outlined in Fig. 4.8 for sequence IIID engine test data obtained using 10W-30 fully formulated oils with different ZnDTP content to which various organocopper compounds at increasing concentrations have been added.

Organocopper compounds inhibit oxidation of thin films of mineral oil (and ester) at 250°C [14, 21]. Under these conditions, polycondensation and polymerisation reactions are suppressed such that only medium-sized, oil-soluble polymers are formed. This leads to an improved control of viscosity [103]. A further stabilisation step, mainly in the upper part of the piston, may result from an interaction

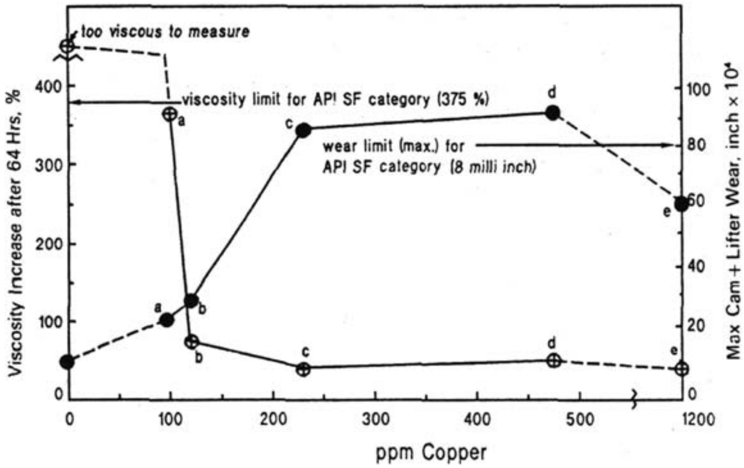


Fig. 4.8 Influence of increasing copper content of different types of organocopper compounds on viscosity ($) and wear (o) in the sequence IIID engine test [102]: (**a**) = 0.156% cupric oleate (94 ppm Cu) + 1.8% ZnDTP; (**b**) = 0.084% cuprous-di-*sec*-hexyl-dithiophosphate (120 ppm Cu) + 1.7% ZnDTP; (**c**) = 0.2% cuprous-di-iso-octyl-dithiophosphate (240 ppm Cu) + 1.65% ZnDTP; (**d**) = 0.39% cuprous-di-iso-octyl-dithiophosphate (486 ppm Cu) + 1.48% ZnDTP; (**e**) = 1.5% cupric naphthenate (1200 ppmCu) + 1.8% ZnDTP

between NO_x, a major contributor to oil degradation, and an organocopper salt, Reaction (4.75):

$$Cu^{1+} + NO_x \rightarrow Cu^{2+} + [NO_x]^- \qquad \text{(Reaction 4.75)}$$

With a rather narrow operating range of 90–120 ppm Cu for organocopper antioxidants in the trade-off between improved oxidation and reduced wear control, the use of organocopper salts has waned as the effectiveness of organomolybdenum compounds has begun to be further explored in modern engine oils.

Organomolybdenum compounds: The most important organomolybdenum chemistries from a commercial point of view are listed under the following generic headings:

a. sulphur-containing compounds based on dithiocarbamates (MoDTC),
b. sulphur- and phosphorus-containing compounds based on dithiophosphates (MoDTP),
c. sulphur- and nitrogen-containing compounds based on dispersants,
d. organomolybdenum compounds free of sulphur, e.g. Mo-carboxylates, Mo-amines/amides.

This set of commercially available compounds represents the evolution of organomolybdenum compounds over the last 30 years. Patents claiming those compounds in combination with all kinds of lubricant additives dominate the patent activity in this field. As a result of the increasing need for improvement in vehicle fuel economy, many international oil marketers use MoDTC at high concentrations, >700 ppm Mo, in their top-tier premium commercial motor oils. An ILSAC GF-3 engine oil formulated with 750 ppm Mo was found to be 0.5% more fuel efficient than the same oil formulated with an organic-type friction modifier additive [104]. Many Japanese OEMs request that their factory-fill engine oils contain this additive technology.

With the advent of the Nissan KA-24-E engine test, ASTM Sequence IV, as part of ILSAC GF-3 in 2000, engine oils containing low concentrations of MoDTC in combination with low levels of ZDDP, 500 ppm, showed excellent control of valve train wear. The data in Fig. 4.9 were reported to the GF-4 ILSAC/Oil Committee 03 to support the use of molybdenum compounds for their supplemental anti-wear capabilities [105].

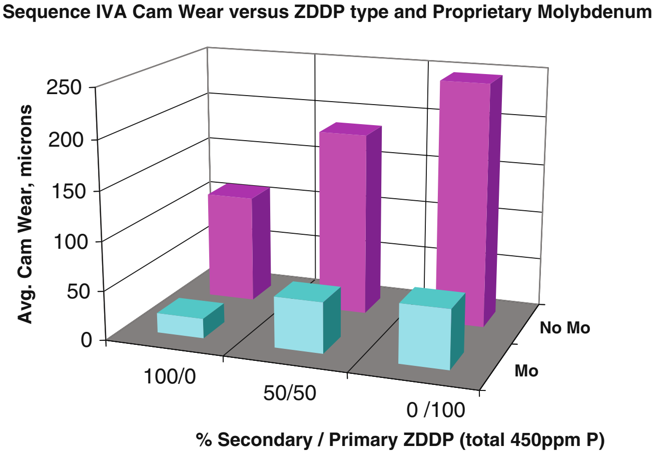


Fig. 4.9 Effect of the use of molybdenum in sequence IVA cam wear

In addition to being good friction modifiers with anti-wear performance, organomolybdenum compounds are also excellent antioxidants at low concentrations, at or below 100 ppm Mo. In fact, over 50% of ILSAC GF-4 engine oils contain organomolybdenum compounds at or above 60 ppm Mo.

Ashless antioxidants: Lack of quality reliability claimed for passenger car engine oils in the United States led to the introduction of ILSAC GF-1 (API SH) for 1994 model year vehicles and the adoption of the American Chemistry Council Product Approval Code of Practice which addresses quality assurance issues. A similar system was adopted later in Europe. With the application of the ACC Code of Practice, the commonly used concentration of alkylated diphenylamine antioxidants in the oil was increased in order to pass Sequence IIIE viscosity control requirements [106]. When the Sequence IIIE, of 64 h test duration, was replaced by the Sequence IIIF, of 80 h duration, with ILSAC GF-3 (API SL) for 2001 model year vehicles, the trend to use higher concentrations of ashless antioxidants continued, especially under the higher temperature conditions and increased lubricant exposure to NO_x in the blow-by gases of the Sequence IIIF engine. In many GF-3 engine oils, higher concentrations of alkylated diphenylamine antioxidants were supplemented with hindered phenolic antioxidants for improved oil resistance to oxidation and nitration.

With the advent of ILSAC GF-4 for 2004 model year vehicles, the Sequence IIIG, of 100 h test duration, replaced the Sequence IIIF and engine oil phosphorus levels were decreased by 20%, from 0.10% maximum to 0.08% maximum. The combination of increased IIIG test severity and decreased ZDDP content was responsible for nearly doubling the level of ashless antioxidant in modern engine oils from pre-2000 levels. Sequence IIIG engine data reported for GF-4 prototype formulations at 0.05%P with additional ashless antioxidant above typical levels used in GF-3 oils is shown in Fig. 4.10 [107]. Significantly more ashless antioxidant, more than three times GF-3 levels, will be needed to control oxidation in oils with 0.05%P from ZDDP.

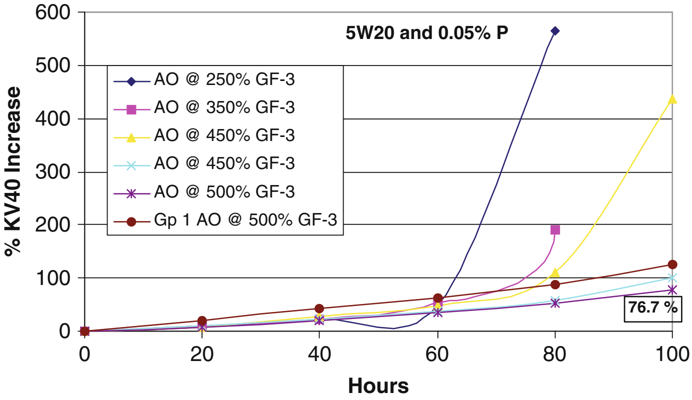


Fig. 4.10 Sequence IIIG viscosity increase vs. time for GF-4 prototype oils [107]

In Europe, the decrease in engine oil phosphorus, sulphur and ash levels (SAPS) with the introduction of ACEA C1, C2, C3 and E6 specifications in 2004, driven by emissions system compatibility, is also responsible for significant increases in the level of ashless antioxidants at the expense of ZDDP, which generally contributes all of the phosphorus, most of the sulphur and some of the ash to most engine oil formulations. Table 4.13 describes the current specified levels of SAPS by ACEA, with ILSAC GF-4 limits added for reference.

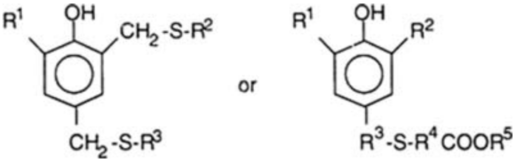
Table 4.13 Current levels of SAPS specified by ACEA and ILSAC GF-4

	ACEA C1 (%)	ACEA C2 and C3 (%)	ILSAC GF-4 (%)
Phosphorus (max.)	0.05	0.08	0.08
Sulphur (max.)	0.2	0.3	0.5
Ash (max.)	0.5	0.8	No limit

In addition, European oil change intervals have increased from 15,000 to 30,000 km with the advent of the ACEA A5/B5 category in 2004, as well as VW 504.00/507.00 and MB 229.5. Extended drain intervals will considerably increase oxidative severity of the engine oil. Indications of how to cope with this increased oxidative severity can be found in a publication [108] which demonstrated that phenolic antioxidants have the most dramatic effect on reducing deposits in a modified panel coker apparatus, which correlated with Sequence IIIE engine tests. This type of ashless antioxidant provides a necessary formulation ingredient in order to meet the requirements of the European engine high-temperature deposit test, TU5JP, the Sequence IIIG piston deposit requirements and also the Thermo Oxidation Engine Simulation Test (TEOST MHT-4).

A different approach to managing viscosity and sludge problems in engine oils has been the use of dispersant–antioxidant–olefin copolymers [109]. The results of IIIE and VE engine tests with an oil containing the dispersant–antioxidant–OCP compared with a dispersant OCP are clearly in favour of the former product. This new product group is synthesised by grafting the antioxidant monomer onto the dispersant OCP. The antioxidant part could be, amongst others, a 2,6-di-*tertiary*-butyl phenol or an alkylated diphenylamine moiety. In the meantime, the concept of grafting antioxidants on to various types of polymer backbones has been adopted [110, 111].

An effective method of sludge reduction in a Japanese engine has been found by adding a bisphenol-type antioxidant to an engine containing a mixture of primary and secondary alkyl ZnDTPs [112]. Also, passenger car lubricant formulations based on sulphur-containing sterically hindered phenols are active at controlling sludge formation even if the phosphorus level of the oil is low [113]. Typical antioxidant structures are the following:



Owing to environmental concerns, fuel economy is gaining momentum. To enhance the lubricant's frictional properties, it is important to minimise the concentration of highly polar oxidation species in the oil as they can compete with the friction modifier for the surface, thereby reducing its activity. These findings support the concept of optimising antioxidant concentrations [114].

4.5.3 Antioxidant Technology for Heavy-Duty Diesel Engine Oils

The present moves to reduce emission limits will continue beyond the year 2010 to ultra-low-emission engines. Engine design change is a decisive factor in meeting these environmental requirements both now and in the future. As a consequence of piston design changes, deposit formation has been observed in low-emission engines [115]. Extended oil drain intervals, up to 100,000 km in Europe, reduced oil consumption, 'dry engines' and the reduction of the sulphur content of diesel fuel down to a level of 15 ppm increase the tendency of deposit formation in the upper part of the piston. Present and future worldwide specifications in the United States, API CJ-4; in Europe, ACEA E6-04 & E7-04, Daimler Benz specification MB 228.5; and in Japan, JASO DH-2-05, place a major emphasis on the control of piston deposits. Any failure in this respect may lead to such deleterious consequences as higher consumption, ring sticking and bore polishing. In Europe, with the extended drain capability of 100,000 km for MB 228.5 engine oils, the control of piston deposits is critical.

Deposits, which are mainly lubricant related, have been described as binders and result from thermal and oxidative degradation of the oil [116, 117]. These binders act as absorbents for fuel combustion products, especially soot. Because high-temperature oxidation processes are the main source of deposit formation, antioxidants, in the form of the more thermally stable primary ZnDTPs, combined with sulphurised alkyl phenols and/or high molecular weight, sterically hindered phenols are able to control this process. A high molecular weight, sterically hindered phenolic antioxidant improves deposit control of an API CH-4 prototype engine oil [118]. The antioxidant, referred to as Antioxidant B, effectively controls piston deposits and top groove carbon at a 0.5% treat rate in the high-temperature Caterpillar 1 N heavy-duty diesel engine test, Table 4.14, which must be passed in order to meet API CH-4 and CJ-4 specifications.

Table 4.14 Deposit reduction of a heavy-duty diesel engine oil containing antioxidant B in the Caterpillar 1 N diesel engine test

Test engine oils Antioxidant B HDD engine oil*	 – Neat	 0.5% Balance	API CG-4 specification 1 run, pass limits
Caterpillar 1 N engine test			
Weighted total demerit (adjusted)	396.2	239.2	286.2
Top groove fill (adjusted %)	19	8	20
Top land heavy carbon	1	0	3
Scuffing, piston	Yes	None	None
Scuffing, rings	Yes	None	None
Scuffing, liner	Yes	None	None
Stuck rings	None	None	None
Average oil consumption	0.31	0.17	0.304 max.

*HDD engine oil formulated for API CG-4 in a solvent-refined oil, without any ashless present, giving a Caterpillar 1 N fail result. Ash content 1%

4.6 Future Antioxidant Technology

ZnDTPs, sterically hindered phenols, alkylated diphenylamines, organomolybdenum compounds and dithiocarbamates are the product groups meeting the present needs of the lubricant industry for the protection of lubricants against oxidation. Will they still be the products in the year 2020? There are important driving forces leading to future antioxidants:

- environmental and emissions concerns,
- improved fuel/energy efficiency,
- higher performance standards,
- new base stocks.

What are the effects of these factors on the selection of antioxidants for industrial and engine lubricants?

4.6.1 Antioxidants for Industrial Lubricants

Presently, there is a strong demand for ‘environmentally acceptable’ fluids. As ‘biolubes’, they need to satisfy biodegradation and bioaccumulation standards, which mineral oil-based fluids cannot achieve. Therefore, the use of synthetic and natural esters for many industrial applications will develop [119]. Not only the base fluids but also the antioxidants used in them will have to fulfil certain specifications for aquatic toxicity, biodegradation and bioaccumulation. Because the antioxidant response of these new fluids is different from mineral oil-based lubricants, new classes of ashless ‘bio-antioxidants’ may need to be developed.

Due to environmental concerns, the majority of ZnDTP-based, anti-wear hydraulic fluids will be gradually replaced by ashless formulations using antioxidant technology, which is environmentally acceptable [120]. The ‘Blue Angel’ specification in Germany for biodegradable hydraulic fluids represents a milestone in terms of toxicity and ecotoxicity requirements for additives, including antioxidants, used to formulate them. Currently, no biodegradable hydraulic fluid meets these criteria.

There is a general trend to reduce the size of industrial equipment without reducing power output. This leads to increased thermo-oxidative stress on the lubricants, which has to be met with more effective antioxidants, i.e. substituting existing antioxidants with lower volatility, higher molecular weight products. Also, poorer quality base stocks will lead to higher treat levels of antioxidants.

4.6.2 Antioxidants for Engine Oils

Lubricants for the next generation of passenger engines will have to cope with increased specific power output, longer drain intervals, reduced oil consumption and especially compatibility with exhaust gas treatment systems and the increased use of biofuels such as FAME (fatty acid methyl esters) and ethanol. Thus, the oil will be exposed to increased temperatures for longer times with higher NO_x concentrations, increased soot levels and increased fuel dilution. Ceramic components will lead to even higher temperatures. Thus, a new antioxidant type will be required which has low volatility, high thermal stability, ability to control future higher NO_x levels in the blow-by and piston cleanliness.

The limitations on particulate emissions, especially in the United States from 2007 onwards, and their strong impact on future engine design raise the question of how future diesel engine oils will be formulated [120, 121]. Ashless antioxidants, leading to improved deposit control and therefore, via reduced oil consumption, to less particulate emission as well as being inherently compatible with exhaust gas treatment systems, could be an important building block. The increased operating temperatures of passenger car and heavy-duty diesel engines will stimulate the use of new lubricant base stocks, e.g. GTL, or gas-to-liquids technology, which will likely require new, tailor-made antioxidants. This trend is expected to be reinforced by the introduction of low-heat rejection diesel engines by the year 2020 [122, 123]. Biodegradable engine oils which have been controversially discussed in the literature [115] are now commercially successful in Europe after the turn of the century. The industry continues to develop proprietary technology, based on ashless antioxidants, anti-wear and friction-reducing additives, and seeks to establish a market position [116].

In summary, antioxidants with improved performance will be a major design factor for future lubricants, operating under more demanding yet environmentally acceptable conditions.

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Chapter 5
Viscosity Index Improvers and Thickeners

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Abstract The viscosity index of an oil or an oil formulation is an important physical parameter. Viscosity index improvers, VIIs, are comprised of five main classes of polymers: polymethylmethacrylates (PMAs), olefin copolymers (OCPs), hydrogenated poly(styrene-co-butadiene or isoprene) (HSD/SIP/HRIs), esterified polystyrene-co-maleic anhydride (SPEs) and a combination of PMA/OCP systems. The chemistry, manufacture, dispersancy and utility of each class are described. The comparative functions, properties, thickening ability, dispersancy and degradation of VIIs are discussed. Permanent and temporary shear thinning of VII-thickened formulations are described and compared. The end-use performance and choice of VI improvers is discussed in terms of low- and high-temperature viscosities, journal bearing oil film thickness, fuel economy, oil consumption, high-temperature pumping efficiency and deposit control. Discussion of future developments concludes that VI improvers will evolve to meet new challenges of increased thermal–oxidative degradation from increased engine operating temperatures, different base stocks of either synthetic base oils or vegetable oil-based, together with alcohol- or vegetable oil-based fuels. VI improvers must also evolve to deal with higher levels of fuel dilution and new types of sludge and also enhanced low-temperature requirements.

5.1 Introduction

The 'viscosity index', VI, was an important measure of quality early in the history of the lubricants industry, indicating an oil's potential applications over a wide range of temperatures, described in Section 1.3.2. Pennsylvania grade oils, ~100 VI, were the standard against which all others were measured. Hydrogenation and solvent extraction processes were developed to upgrade lubricants from poorer quality crude oils, but the practical VI ceiling for 1930s refinery technology was ~110–115.

Early workers found that small amounts of rubber dissolved into mineral oil substantially raised VI; however, high levels of unsaturation in the polymer led to oxidation and sludge formation. This was overcome by using a synthetic polymer prepared from gasoline light ends [1], and similar behaviour was later described for

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polymethacrylates [2, 3] and polyisobutylene [4, 5]. As these materials were initially and primarily used to increase the viscosity index, they became known as ‘viscosity index improvers’, or VIIs.

The SAE 10W and SAE 20W requirements in the Automotive Manufacturers’ Viscosity Classification in 1941 created the possibility of formulating an oil to meet the requirements of more than one SAE grade. Formulation of ‘double graded oils’ with polymethacrylates, including an SAE 10W-30 oil, ‘might well be called an all season motor oil’ [6]. Rapid exploitation of VI improvers for the development of multigrade engine oils followed during the 1950s.

Whilst engine lubricants are, by far, the largest commercial application of VI improvers, they are also widely used in other lubricant formulations. These include automatic transmission fluids, multipurpose tractor transmission fluids, power steering fluids, shock absorber fluids, other hydraulic fluids (industrial, automotive, off-highway, aircraft), manual transmission fluids, rear axle lubricants, industrial gear oils, turbine engine oils (both stationary and aircraft) and aircraft piston engine oils. Many of these application fluids have special needs, as will be shown in the following sections.

5.2 An Overview of VI Improver Chemistry

Since the early developments with polymethacrylates and polyisobutylenes, a wide variety of polymers have been explored. All of these have been developed at least to the point of commercial sampling; examples are shown in Table 5.1. Five core technologies currently find important commercial usage:

- polymethacrylates, generally referred to as PMAs,
- poly(ethylene propylene) and closely related modifications, referred to as ‘olefin copolymers’ or ‘OCPs’,
- hydrogenated poly(styrene-co-butadiene or isoprene) and their modifications HSD or, in the case of isoprene, SIP, together with star-shaped polymers based on radial hydrogenated polyisoprene (HRI) which has largely supplanted the older HSD/SIP chemistries,
- esterified poly(styrene-co-maleic anhydride), normally and incorrectly described as styrene polyester, or SPE,
- and a combination of the first two, concentrate-compatibilized PMA/OCP systems.

Only these five will be described in detail in the following section, and simplified chemical structures of the four basic technologies are given in Fig. 5.1. Some VI improver compositions have pour point depression activity and/or dispersancy, in addition to their basic viscosity control properties. The former are described as appropriate in the following sections but are described in greater detail in Section 6.2.

Table 5.1 Representative VI improver chemistries

Polymerized light mixed olefins
Polyisobutylene
Polymethacrylates
Polymethacrylates-co-acrylate
Polymethacrylates-co-styrene
Polybutadiene
Alkylated polystyrene
Poly(*t*-butyl styrene)
Poly(alkyl fumarate-co-vinyl acetate)
Poly(*n*-butyl vinyl ether)
Esterified polystyrene-co-maleic anhydride
Polyethylene-co-propylene
Poly(ethylene-co-propylene diene-modified)
Poly(ethylene-co-propylene-co-olefin diene-modified)
Hydrogenated polystyrene-co-butadiene
Hydrogenated polystyrene-co-isoprene
Hydrogenated polyisoprene.

Dispersant VI improvers are used to a certain extent in engine oils but are more often used in automatic transmission fluids and multipurpose tractor fluids. Incorporating dispersancy into a polymer requires carefully engineered addition of a strongly polar functional group to the base polymer backbone. The most commonly employed functional groups are amines, alcohols or amides. Their mode of incorporation depends largely on the base polymer, and specific details will be described later.

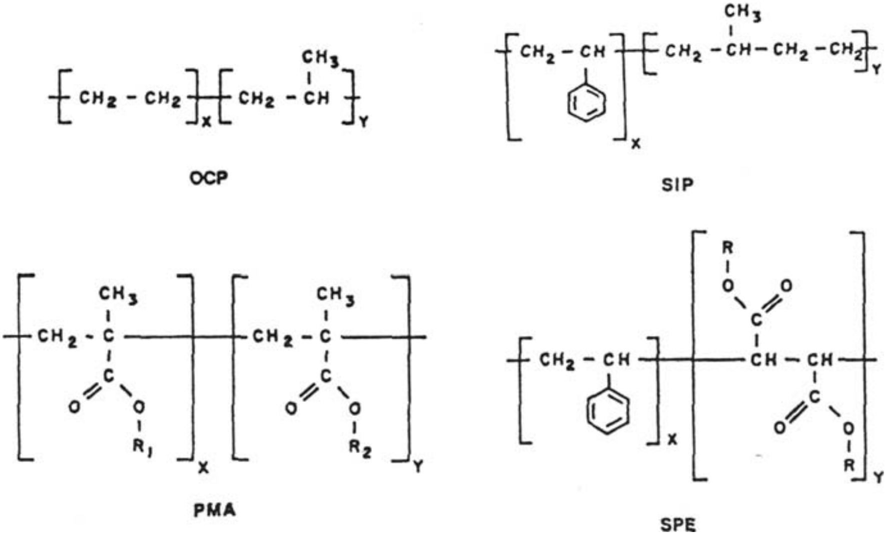


Fig. 5.1 Simplified chemical structures of major VI improver classes

5.3 Chemistry and Manufacture of Commercial VI Improvers

The three most important commercial VI improver families each represent one of the most important commercial techniques for manufacturing high molecular weight polymers, thus polymethacrylates by free-radical chemistry, olefin copolymers by Ziegler chemistry and hydrogenated styrene–diene or copolymers by anionic polymerization.

5.3.1 Polymethacrylates – Chemistry

Polymethacrylate VI improver chemistry has been extensively reviewed [7–10]. Polymethacrylate-based VI improvers used in engine oil are usually copolymers of three methacrylic acid esters: short-, intermediate- and long-chain alkyl methacrylates. Both methyl and butyl (*n*-butyl, isobutyl or mixtures of the two) methacrylates have been used for the low-alkyl component, although methyl methacrylate is by far the most common. The intermediate alkyl radical can vary widely but is normally derived from a group including 2-ethylhexyl alcohol, isodecyl alcohol and alcohol mixtures which may be C_8–C_{10}, C_{12}–C_{14} or C_{12}–C_{15}. The long-chain alkyl esters are based on either C_{16}–C_{18} or C_{16}–C_{20} mixtures. Any of the alcohols in the C_{12}–C_{20} range may be derived from either natural or synthetic sources. All of the intermediate- and long-chain alkyl esters are made commercially by either acid-catalyzed direct esterification of methacrylic acid or trans-esterification of methyl methacrylate.

The ratio of the three monomers is normally chosen such that the average alkyl side chain count is about nine carbon atoms. To a first approximation, the viscosity–temperature properties of the copolymer will be the same, independent of the combination of alkyl groups chosen to reach the average. The preferred combination is determined by its wax-interaction properties, where linear alkyl groups of 14 carbon atoms, or more, interact with wax so that polymethacrylates are frequently designed to incorporate a pour point depression function into the VI improver molecule. If the high molecular weight alkyl methacrylate is used in combination with a mid-cut which has no linear C_{14} or larger, it will be used at a higher concentration than in the reverse situation where the mid-cut can carry some of the wax-interaction burden.

For non-engine oil applications, the compositions are optimized for the particular lubricant base stock as well as any specific needs of the end use. Most often these involve rebalancing polymer solubility and elimination of the high-alkyl monomer, where wax interaction is not an issue, as for synthetics or naphthenic mineral oil base stocks.

Manufacture: Polymethacrylate VI improvers are free-radical initiated solution copolymers. A wide variety of peroxide or azo initiators may be used, and several are used commercially, choice dictated largely by half-life at reaction temperatures in the range 100–140°C. In turn, this is driven by manufacturing convenience and kettle productivity factors. Production is a simple batch or semi-batch process at a theoretical polymer content of 50–90%, the solids level dependent upon both the polymer molecular weight and the mixing capabilities of the system.

The process solvent is usually mineral oil in a viscosity/volatility range compatible with the use of the end product. Volatile solvents such as toluene have been used commercially, in which case the final process step is a solvent–oil exchange. The primary criteria for a solvent are relative freedom from significant chain transfer activity and a boiling point compromise between the reaction temperature and ease of solvent transfer at the end of the reaction.

The products produced are random copolymers. No special steps are necessary to achieve this distribution since reactivity ratios of all of the alkyl methacrylate monomers are almost the same. Processes may include special conditions to help minimize molecular weight distribution. VI improvers for engine oils have a molecular weight, M_w, between 250,000 and 750,000 amu with an M_w/M_n distribution between 3 and 4. The products are sold commercially as concentrates ranging from 35 to 55% polymer, entirely a practical matter dictated by handling characteristics. The molecular weights for other applications range down to about 30,000–40,000 amu with product solids ranging up to ~70%.

Dispersancy: Solution copolymers are comparatively easy to produce in dispersant form as copolymerization with an appropriate polar monomer is relatively straightforward. If the polar monomer is also a methacrylate, reactivity ratios are essentially the same and no special procedures are required to produce random copolymers. Commercial examples have included dimethyl (or diethyl)aminoethyl methacrylate [11], hydroxyethyl methacrylate [12] and dimethylamino-ethyl methacrylamide [13]. 2-Methyl-5-vinyl pyridine [14] has also been used commercially, reactivity ratios are such that it copolymerizes slightly faster than alkyl methacrylates. Although composition drift is not severe, it should be added in a programmed fashion if a uniform distribution is desired. *N*-vinyl pyrrolidinone, in contrast, copolymerizes very sluggishly with methacrylates and is best incorporated via a graft reaction [15], sometimes also grafted in combination with *N*-vinyl imidazole [16]. Since solution chemistry is used to produce dispersant polymethacrylates, like preparation of the base polymer, only relatively simple process modifications are necessary to produce dispersants commercially.

Utility: Because free-radical solution chemistry can produce a broad range of molecular weights and compositions, polymethacrylates are used in almost all lubricant areas where viscosity/temperature modification is required. This includes both mineral oil-based applications and a range of synthetic fluids.

5.3.2 Olefin Copolymers: Chemistry

The chemistry of ethylene–propylene-based VI improvers has been extensively reviewed [17–20]. Olefin copolymer-based VI improvers are primarily derived from ethylene and propylene. However, some commercial examples are also diene-modified, the so-called EPDMs, whilst still others contain two diolefins. Since their solution rheology is dictated almost exclusively by the ethylene and propylene content, the diene modifications relate primarily to bulk handling characteristics, as will be noted later. In some cases, EPDMs may be somewhat more reactive towards functionalization, but by the same note, they are slightly less stable towards oxidation than poly(ethylene–co-propylene). The ter- and tetrapolymers also tend to be less efficient thickeners than the copolymers.

Ethylene contents of OCP VI improvers are normally in the 40–60 wt% range (50–70 mol%), generally lower in ethylene content than the EP copolymers used in most other applications. The ethylene/propylene ratio for VI improvers is a compromise between thickening efficiency and low-temperature solubility. The best thickening effect is achieved at high ethylene content, but too much ethylene leads to polymer crystallinity and insolubility at low temperatures. Copolymers with excessively high ethylene contents can interact with mineral oil wax at low temperatures with devastating effects on low shear flow. A further consideration in choosing the ethylene–propylene ratio is the objective of minimizing propylene content to achieve the best possible oxidative stability. Another concern is the sequence distribution of ethylene and propylene units in the polymer. Microcrystalline regions resulting from runs of ethylene units can also interact with wax at low temperatures, resulting in undesirable low-temperature properties needing a compromise between thickening efficiency and low-temperature viscometrics [21]. OCP VI improvers have normally been prepared by techniques which maximize the random distribution of the two monomer units. However, more recent technology has given tapered compositions, as controlled intramolecular monomer unit distributions, which are excellent thickeners with improved low-temperature properties and able to avoid undesirable wax interactions.

The ethylene–propylene ratios of EPDM-based VI improvers have the same range as the above OCPs. The dienes used must be non-conjugated, with only one reactive double bond, the most common options being 1,4-hexadiene, 5-ethylidene-2-norbornene and dicyclopentadiene, used at relatively low levels of ~2–5%. This is lower than EPDMs for most other applications, the final level being driven primarily by negative effects on thickening efficiency, cost and oxidative stability. The OCP tetrapolymers are also EPDM-based but include a second diolefin where both double bonds are reactive, such as 2,5-norbornadiene used at very low levels, <1.0%, to introduce a small amount of branching into the polymer [22]. The resulting polymers have better handling characteristics as solids, as discussed later, but achieved at the expense of reduced thickening efficiency. The molecular weight of OCP VI improvers is 50,000–200,000 amu with molecular weight distributions, M_w/M_n, of ~2.0–2.5. The newer tapered compositions tend to be slightly higher in molecular weight with narrower molecular weight distributions of less than 2.0.

Manufacture: Olefin copolymer VI improvers are produced by solution polymerization of ethylene and propylene catalyzed by soluble Ziegler–Natta catalysts. The most commonly used catalysts are an aluminium alkyl halide with a soluble vanadium compound. Heterogeneous catalysis can also be used, but the polymer properties are less desirable for VI improver use. Polymerization is carried out in relatively dilute hexane solution at low temperature. Excess ethylene and propylene are removed and the solutions washed with water to coagulate the polymer and also to remove catalyst residues. The polymer is then dried and baled in convenient size blocks for further handling.

Metallocene catalysis is an alternative to the traditional Ziegler–Natta vanadium-based catalysis for commercial polyolefin production, e.g. the use of metallocene-catalyzed ethylene alpha-olefin copolymers as viscosity index modifiers for lubricating oil compositions [23]. The catalyst is an activated metallocene transition metal, usually Ti, Zr or Hf, attached to one or two cyclopentadienyl rings and typically activated by methylaluminoxane. Metallocene catalysis achieves more stereo-regularity and also enables incorporation of higher alpha-olefins and/or other monomers into the polymer backbone. In addition, the low catalyst concentration does not require a cleanup step to remove ash.

Since the polymers for VI improver use are lower in both molecular weight and ethylene content than similar polymers for other applications, the bulk polymers are extremely tacky, making handling an issue. Several options are practised commercially to minimize the tack/melt flow problem; the most widely practised option is to produce a higher molecular weight polymer than required for VI improver use and then to degrade it, mechanically and/or oxidatively, in the dissolution step. This is achieved by mastication in intensive mixers such as Brabender mixers or extruders. A second option is to produce either a diene-modified polymer or a tetrapolymer, but performance and cost limitations mentioned earlier limit this technique. Incorporating the second diolefin is particularly effective for improving the melt flow behaviour but with significant loss in thickening efficiency. The other alternative is a simple solvent transfer to oil during the isolation step which eliminates solid handling so that melt flow is not an issue. The polymer is made at the correct molecular weight, and further processing is avoided. These apparent advantages must be balanced against the potential advantage of shipping solid polymer over long distances.

OCP VI improvers are sold both as solids, typically as bales of ~20/35 kg wrapped in polyethylene and, more commonly, as concentrated solutions in mineral oil. They are excellent thickeners in the bulk phase, and polymer content is limited by handling considerations to ~6–15%. OCP VI improvers are not in themselves pour point depressants, but pour-depressant versions are often sold as physical mixtures of OCP VI improver with 2–3% of conventional pour point depressant included in the concentrate.

Dispersancy: Incorporating dispersancy into OCP VI improvers is considerably more difficult than the case with free-radical solution chemistry, as described for PMAs. Direct copolymerization of the preferred N- or O-containing monomers is not practical since these Lewis bases will complex, and thus poison, the acidic Ziegler–Natta catalysts. The only option identified so far is to use an amount of catalyst in excess of that complexed by the polar monomer, as described for *N*-vinylimidazole [24] or *N*-vinyl succinimide [25].

In spite of this, there is no shortage of technologies for synthesizing dispersant OCPs. All of the useful techniques focus on reactions of the polymer involving attack at the most reactive positions, either the propylene tertiary hydrogen atom in the case of OCP copolymers or that plus the unsaturation and/or allylic hydrogens in EPDMs. The easiest attack on these sites is simply oxidative degradation to give a complex mixture of aldehydes, ketones and acids which can then serve as reactive sites for other reactions. This mixture can be reacted with amines directly, which has not proved to be a very useful technique, or can be used in a Mannich condensation [26].

The most successful route, and most widely practised commercially, is graft polymerization, where the grafts are grown following hydrogen abstraction, presumably again at the propylene site. Grafting at the allylic position to the unsaturation in an EPDM would appear to be an attractive option, but evidence is lacking that this is the preferred site, perhaps simply because of mass effects; that is, the greater reactivity is overshadowed by very low concentrations. For practical reasons, the solvent of choice for the graft process is mineral oil, where mixing considerations normally dictate that the system should contain about 60–80% oil. Hence, direct hydrogen abstraction or chain transfer to oil are important side reactions limiting the yield of the desired polymer graft. The chemistry works extremely well in a non-chain-transfer solvent, such as chloro- or dichlorobenzene [27], but this introduces solvent transfer and recovery problems. A process has also been described for grafting in the absence of solvent [28].

In spite of these problems, graft processes have been practised commercially both in solvent and oil. Successful examples have included both 2-vinylpyridine and *N*-vinyl pyrrolidinone grafts [29]. Maleic anhydride has also been grafted, but this route requires an additional step to further functionalize the anhydride. Amines, for example, *N*-(3-aminopropyl)morpholine [30], are most commonly used to form the corresponding imide. The use of polyamines, such as diethylenetriamine, has also been described, but these tend to crosslink and the terminal amine must be capped as amide [31] or imide [32]. The terminal amine in polybutene-based succinimide ashless dispersants has also been reacted successfully with the anhydride [33]. Another important functionalization technology is grafting OCP to provide succinic anhydride sites for further reactivity with a mixture of antioxidant compounds [34]. The specific compounds are aminoalkyl phenothiazine and *N*-phenyl-*p*-phenylene diamine, giving a dispersant and antioxidant VI improver product. The preceding options focused on those routes which are, or appear to have the potential to be, commercial. The patent literature contains numerous other examples, most of which are at this point technical curiosities.

Utility: The excellent thickening ability of OCPs has led to their extensive use in engine oils, both diesel and gasoline. However, the relatively poor low-shear, low-temperature viscosity behaviour of OCPs together with difficulty of achieving the necessary lower molecular weights (better shear stability) have precluded significant use in most other speciality lubricants.

5.3.3 Hydrogenated Styrene–Diene Copolymers and Radial Isoprene: Chemistry

The chemistry and performance features of hydrogenated styrene–diene VI improvers has been reviewed [35], with several subclasses covering either butadiene or isoprene as the diene, and either random, block or star-shaped polymers. The basic member is a random copolymer of styrene and butadiene [36, 37], containing ~50–60 wt% styrene and ~40–50 wt% butadiene. For optimum thickening, the butadiene should polymerize with a high 1,4-configuration content. However, to prevent linear polyethylene-like regimes and the associated problems similar to those described for OCPs, 30–40% of the butadiene in the product has a 1,2-configuration. The final products are obtained by hydrogenation using a technique giving very high conversion on the butadiene-derived unsaturation whilst hydrogenating little or none of the styrene. Molecular weights can be in the range of 75,000–200,000 amu with M_{w}/M_n distributions of less than 1.5.

Both diblock, A–B, and triblock, A–B–A, polymers are used commercially, where A represents polyisoprene and B represents polystyrene [38, 39]. A high yield of the 1,4-isoprene configuration is desirable for maximum thickening efficiency. Hydrogenation, again, is nearly complete on the isoprene-derived unsaturation and negligible on styrene. Since the polystyrene regimes are oil insoluble over most of the relevant temperature range for engine oils, these block polymers function as associative thickeners. Thus, the molecular weights of the individual molecules tend to be on the low side with the styrene block having M_{w}s of 10,000–50,000 amu and the isoprene blocks in the range of 50,000–100,000 amu.

Several star-shaped molecules have also been described [39], but the most common one involves hydrogenated isoprene arms in the range of 5–15 on the divinylbenzene-based core. The divinyl benzene content depends on the molecular weight but is typically quite low, e.g. less than 1%. Since these structures represent a compromise between thickening ability and shear stability, their molecular weights tend to be higher than other members of this class, falling in the range 300,000–700,000 amu with molecular weight distributions under 1.5. These star-shaped polymers may also incorporate some styrenic end caps [40].

The radial isoprenes and variations have largely supplanted the diene–styrene block technologies in commercial applications. The relative lack of large, styrene blocks in polydiene star-shaped polymers relative to the block copolymers leads to a relative lack of associative thickening and hence different behaviour under high-shear-rate conditions. In addition, the morphology of the polydiene stars are reputed to provide good permanent shear stability properties as the shearing off of an arm still leaves a polymer coil with a relatively large hydrodynamic volume.

There is one additional group of polymers which is derived from this chemistry, the hydrogenated polydienes. Hydrogenated polyisoprenes [41] are chemically equivalent to an alternating copolymer of ethylene and propylene when polymerized in a 1,4 configuration and would thus be expected to exhibit behaviour which is very similar to that of OCPs. Similar characteristics can be achieved with polybutadiene provided that the 1,2 content is above ~30% [42]. Combinations of butadiene and isoprene have also been patented [42].

Manufacture: Styrene–diene copolymers are produced by anionic solution polymerization, typically using *s*-butyl lithium in cyclohexane at 60–120°C. The system may also be promoted by small amounts of an amine such as *N*,*N*,*N*′,*N*′-tetramethylethylene diamine or an ether, such as tetrahydrofuran. Polymerization solids are in the range of 20–25%.

For random polymers, all of the monomers may be charged together. However, the steps are sequenced for blocks and stars. For blocks, one of the monomers is polymerized, and then the second is added to the living polymer to make an A–B block. In the case of stars, the arms are polymerized first and then divinyl benzene is added to the living polymer arms to form the basic structure. The living polymer is then terminated by addition of an alcohol or by the subsequent hydrogenation. The polymers are hydrogenated in solution using a homogeneous catalyst such as trialkyl aluminium and an organo-nickel compound, such as nickel octanoate or acetylacetonate. Finally, the polymers are washed with water to remove the salts and to coagulate the polymer. Since these polymers do not have the melt flow problems associated with OCPs, either the products are isolated as granules or the granules may be compressed into bales. Hydrogenated styrene–diene VI improvers are sold in both of these solid forms as well as in oil concentrates of ~6–20% solids content. Associative thickeners must be handled in the low solids range, while the other polymers may be on the higher side.

Dispersants: There are currently no commercial examples of dispersant hydrogenated styrene–diene VI improvers. However, several options are described in the patent literature. Any polar monomer which can polymerize readily by an anionic process, such as any of the vinyl pyridine family, may obviously be included directly in the VI improver backbone, most often as a block [43]. As a practical matter, any monomer used in this fashion must also be completely free of impurities which could serve as a source of protons, thus terminating the living polymer. A second technique, unique to this family, involves metallation of the backbone by reaction with butyl lithium followed by growing a graft by an anionic mechanism [44]. This may be the preferred route since addition of vinyl pyridine to the original living polymer decreases the hydrogenation rate considerably. Similarly, there are no commercial examples of dispersant star-shaped polymers, but there are patent descriptions [44], of *N*-vinyl imidazole grafted to either blocked styrene–diene copolymer or star-shaped diene–styrene. This free-radical grafting technology also represents another potential avenue to other dispersant structures, but the chemistry completely parallels the OCP options discussed earlier.

Utility: Hydrogenated styrene–diene and star-shaped diene VI improvers have found their widest utility in gasoline and diesel engine oils. They may also be used in other applications which have only moderate requirements for shear stability, such as tractor transmission fluids and aircraft piston engine oils. However, the shear stability demands of many of the specialty applications precludes the use of currently available products.

5.3.4 Styrene Polyester: Chemistry

This family of VI improvers are styrene–fumarate copolymers from the esterification of an ~1:1 styrene–maleic anhydride copolymer [45]. Only dispersant versions are available, the dispersancy provided by either an amide or, more likely, the imide derived from *N*-(3-aminopropyl)morpholine. Molecular weights, M_w, are in the range of 350,000–700,000 with M_w/M_n of ~3–4.

Manufacture: The copolymer of styrene–maleic anhydride is slurried in mineral oil and esterified to about 70% with a C_{8-18} alcohol mixture, using an acid catalyst at 150–160°C. Esterification is then carried to 95% using *n*-butanol. *N*-(3-aminopropyl)-morpholine is finally added to react with the remaining acidity. The final product is sold as a 35–45% polymer concentrate.

Utility: These products are used almost exclusively in automatic transmission fluids and multipurpose tractor fluids; however, these uses are apparently diminishing in favour of polymethacrylate chemistry.

5.3.5 Concentrate-Compatible PMA/OCP Blends – Chemistry

These products are a blend of conventional PMA and OCP VI improvers [27, 46]. The two polymers are normally incompatible in concentrated form but have been made compatible by incorporating a small amount of a polymethacrylate–OCP graft copolymer. The final product is normally ~65% PMA and ~35% OCP of polymer solids. In the concentrate, the more solvent-like polymer exists as a continuous phase, while the other is in a discontinuous, micellar phase. For that reason, the concentrate is sold in a mineral oil carrier to which a polar solvent such as an ester or ethoxylate is added at ~5% to invert the two polymer phases. The PMA becomes the continuous phase and the OCP the discontinuous phase. As a result of having the poorer thickener in the soluble phase and the better thickener dispersed, a higher solids content can be achieved at handling viscosities than would otherwise be the case. The solids content is in the region of 40%. Further evolution of the concentrate-compatible art describes stable blends of 55% polymer solids with an even higher OCP polymer content of 70 and 30% PMA [47]. Molecular weight and molecular weight distributions of the two components are in the conventional ranges for their classes.

Manufacture: A conventional methacrylate monomer mixture is polymerized by free-radical initiation in an oil solution of about 10–15% of an OCP VI improver at a temperature of 120–140°C. This part of the reaction is carried out at a fully converted polymer solids content of 40–50%. When methacrylate conversion is complete, additional solid OCP VI improver is added to bring the total OCP content up to the desired level. The final product is then diluted with ester solvent to invert the phases, and sufficient additional mineral oil is added to reach the final product solids.

Dispersancy: Dispersancy may be incorporated by any of the means described above for PMA or OCP. Currently only grafting with *N*-vinyl pyrrolidinone or an *N*-vinyl pyrrolidinone/*N*-vinyl imidazole mixture is practised commercially, conducted after the addition of OCP in the reaction sequence described above.

Utility: These products are only used commercially in gasoline and diesel engine oils. As described previously, inclusion of OCP precludes use in most other applications.

5.4 Function and Properties

5.4.1 Solution Properties

Although polymer treat rates in multigrade oils fall into what may be described as the semi-dilute solution regime, dilute solution theory has been useful in describing VI improver behaviour. VI improvers follow the well-known dilute solution behaviour described by Huggins, Equation (5.1), and Kraemer, Equation (5.2), reasonably well, with concentrations normally in a range where terms higher than second order are negligible. An exhaustive study of the application to PMA VI improvers has been published [48], including determination of the values of k' and k'' for several systems:

$$\eta_{\mathrm{sp}}/c = [\eta] + k'[\eta]^2 c + \cdots \qquad \text{(Eqn. 5.1)}$$

$$\ln \eta_{\mathrm{r}}/c = [\eta] - k''[\eta]^2 c + \cdots \qquad \text{(Eqn. 5.2)}$$

Useful relationships are derived from these equations by working first with the Kraemer equation, rearranging and substituting from the Mark–Houwink equation, $KM_{\mathrm{v}}{}^{\mathrm{a}}$ for $[\eta]$, gives Equation (5.3),

$$\ln \eta = KM_{\mathrm{v}}{}^{\mathrm{a}}c - k''(M_{\mathrm{v}}{}^{\mathrm{a}})^2 c^2 + \ln \eta_{\mathrm{o}} \qquad \text{(Eqn. 5.3)}$$

which indicates that the viscosity of an oil solution, η, should increase logarithmically with polymer concentration, c, and also with viscosity average molecular weight, M_{v}, and therefore weight average molecular weight, M_{w}, to a first approximation, raised to the power a. The relationship has an intercept at log (base oil viscosity), η_{o}.

In practice the relationship allows the investigator to create a fair understanding of the viscosity–concentration relationship for a given polymer–oil combination with a single blend. The complete relationship is given by two or three blends to define the curvature introduced by the second-order interaction. Further, oils which are chemically similar enough to have the same K and a values will define a series of parallel lines with intercepts at ln η_{o}. Better solvents have steeper slopes because of the higher a values. The validity of all these relationships is shown graphically in Fig. 5.2.

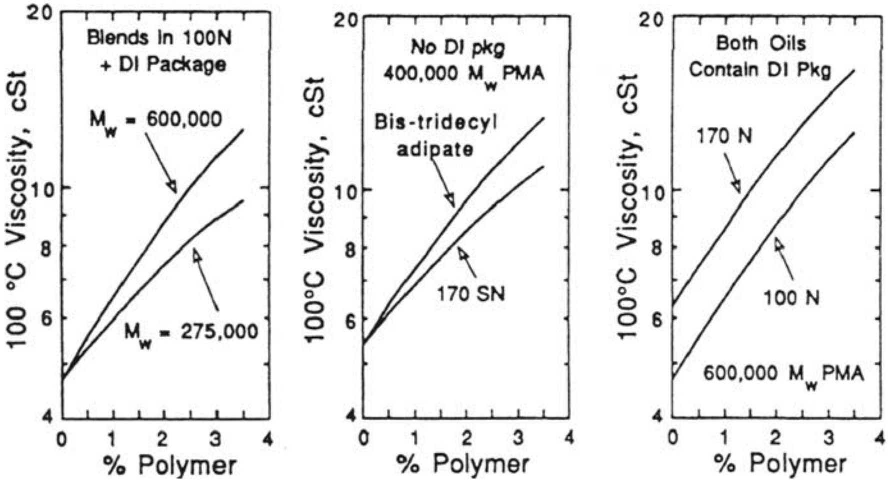


Fig. 5.2 Effects of molecular weight, base stock type and base improver thickening efficiency

Combining the Huggins and Kraemer equations and substituting $KM_V{}^a$ for $[\eta]$ gives the relationship for thickening a specific base oil to a specific blend target, Equation (5.4),

$$\log c = -a \log M_V + K_S \qquad \text{(Eqn. 5.4)}$$

K_S is a very complex constant, containing the constants for polymer interaction, k' and k'', from both the Huggins and Kraemer equations, K from the Mark–Houwink equation, as well as both the base oil and blend viscosities. This log–log relationship is verified for polymethacrylates, Fig. 5.3.

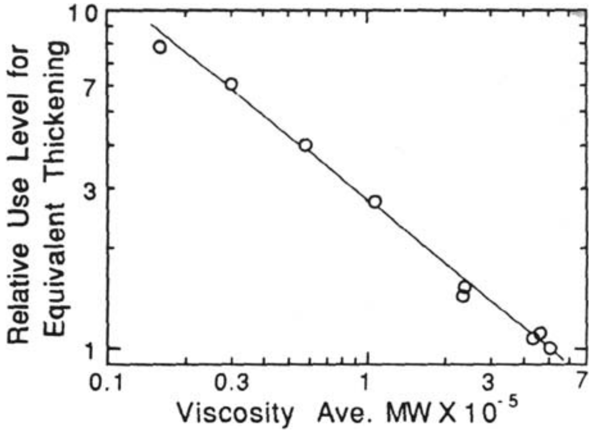


Fig. 5.3 Relationship of PMA thickening efficiency to molecular weight

In terms of chemistry, it is important to note that the intrinsic viscosity, [η], or some other measure of molecular dimensions in solution, is the driving force in thickening efficiency, not the molecular weight per se. In other words, it should not be expected that two chemically different polymers of the same molecular weight will thicken in the same way. Indeed, if chemical structures are radically different, it is virtually certain that they will not.

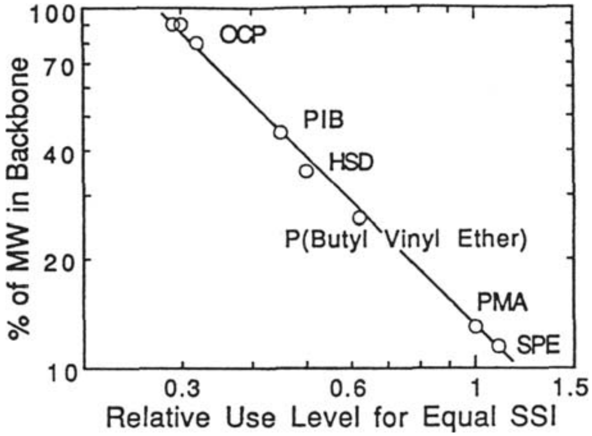


Fig. 5.4 Relative thickening efficiencies of various VI improvers

For high molecular weight polymers, the unperturbed mean square end-to-end distance in solution is a function only of the degree of polymerization and is independent of the presence or absence of side chains. For example, addition of long alkyl side chains to the PMA is necessary to make a soluble polymer, but they contribute nothing to thickening ability, [η], root mean square end-to-end distance or whatever measure of size in solution may be chosen. In turn, then, the relative thickening efficiency across polymer chemistry is a function of the percentage of the mass of that molecule which is in the backbone, Fig. 5.4, noting that this takes the same form as the relationship shown in Fig. 5.3.

Whilst this description is useful to understand the general concepts involved, it must be recognized as only a first approximation to thickening. It is derived from thickening as measured by kinematic viscosity at 100°C and makes no allowance for extensive long-chain branching, dramatic differences in molecular weight distribution, associative thickening or other special effects.

5.4.2 Mechanism of Function

The preceding discussion of thickening described some of the factors involved with thickening at 100°C, an extremely important issue since this strongly influences level of use and, therefore to a large degree, formulation economics. However, since a VI improver must work over a large temperature range, a further factor of interest is how viscosity varies with temperature.

Looking back to dilute solution theory, the issue falls back to the temperature dependence on k' and/or k'' in the Huggins and Kraemer equations, respectively, as well as K and a in the Mark–Houwink equation. These, in turn, relate in a complex fashion to other basic physical chemical parameters. It was hypothesized that the mode of action focused on the hydrodynamic volume of the molecule as a function of temperature [49], where the molecular size in solution was highly contracted at low temperature, thus contributing little to viscosity. But at high temperature, it was greatly expanded, thus making a large contribution. However it was reported that of the three major VI improver classes in use today, only PMAs exhibit an intrinsic viscosity which increases uniformly with increasing temperature. The two hydrocarbon VI improvers tend to either exhibit a uniformly decreasing intrinsic viscosity with temperature or go through a maximum somewhere in the relevant temperature range, Fig. 5.5.

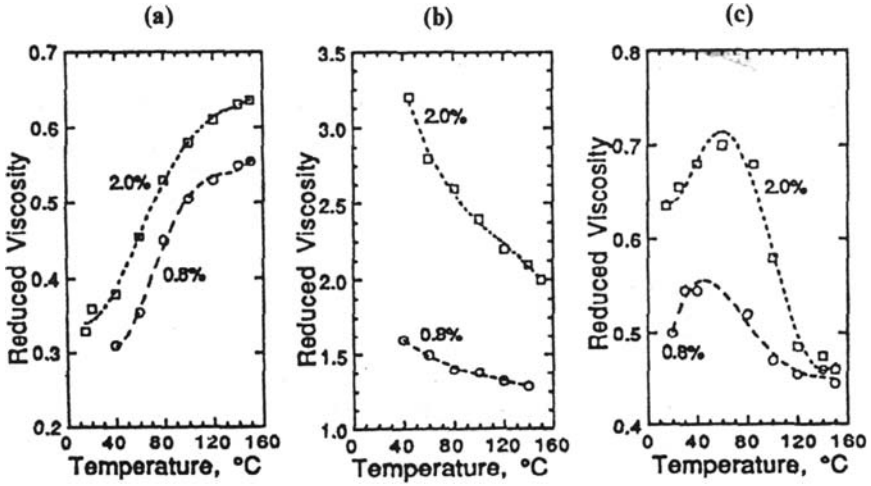


Fig. 5.5 Temperature dependence on polymer coil dimensions for major VI improver chemistries: (**a**) PMA, (**b**) OCP and (**c**) HSD [50]

The effect of temperature on the flow behaviour of polymethacrylate and polyacrylate blends in mineral oil demonstrated that it is strongly controlled by the entropy of activation for viscous flow [51], confirming early speculations [52]. The increased negative entropy was presumably a result of the very sluggish translational motion of the polymer coils. On the other hand, the enthalpy of activation for viscous flow of the polymer solutions was, for the most part, very nearly the same as that of the oil solvent. Only the most efficient systems exhibited decreased enthalpy, suggesting that coil expansion at high temperatures may be a factor, but the effect was very small relative to the entropy effect.

Similar observations were made for a polymethacrylate VI improver in both a light paraffinic and a light naphthenic oil [53]; however, it was reported that both the flow activation enthalpy and entropy increased for polyisobutylene solutions. This apparent anomaly is explained when it is noted that the PIB molecular weight used in this study was only 930 amu, well below that for a VI improver. The result for this low molecular weight PIB was entirely consistent with other observations for heavy base oils of high VI [51]. The effect of VI improver on the translational mobility of solvent molecules, studied by NMR, showed progressive reductions in translational mobility with increasing polymer concentration in both *t*-butylbenzene and *t*-butylcyclohexane [54]. Furthermore, the self-diffusion coefficient of polymer-containing solutions does not increase as rapidly with increasing temperature from 40 to 110°C, as it does for the solvent itself. But it should be noted that the viscosity–temperature relationships considered here barely address the problem. High-temperature specifications are increasingly focused on high-shear-rate viscosity at temperatures of 125–175°C, whilst at low temperatures, both high- (cranking) and low-shear rates (pumping) are of concern. Furthermore, low-temperature viscosities are greatly complicated by the presence of wax.

5.4.3 Shear Stability: Permanent Viscosity Loss

When polymers are subjected to a high shear stress in equipment, the random coil is severely distorted. In extreme cases, bond energies can be exceeded, and the polymer will break, or shear, as shown schematically in Fig. 5.6. This can happen in

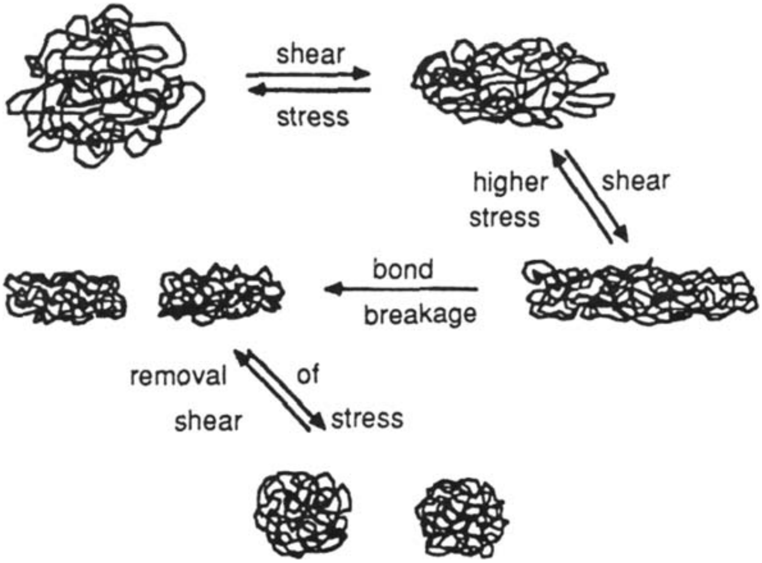


Fig. 5.6 Schematic of mechanical polymer degradation

a variety of areas in equipment, for example, between piston rings and a cylinder wall, between cam and follower in the valve train of an engine, between gear teeth or across the pressure relief valve of a hydraulic system.

The shearing process itself is a simple homolytic scission of a carbon–carbon bond to produce two polymeric radicals. There is no evidence that these radicals are involved in other aspects of lubricant chemistry and are apparently rapidly terminated by either antioxidant or other species in the oil. Backbone carbon–carbon bond strengths of all of the VI improver are much the same so none of the chemistries is inherently more stable than any other. Several workers have proposed that at least some of the shearing takes place at weak links, such as might result from steric hindrance, but there is little or no evidence to support this hypothesis.

If the polymer is stretched, theory predicts that the maximum energy is concentrated in the middle of the molecule, or at least, well away from its ends. Thus, when a polymer is sheared mechanically, the two resulting fragments are predicted to be about half the molecular weight of the starting polymer [55]. It was hypothesized that the fragments need not be the same molecular weight, but smaller pieces would be no less than half of the limiting molecular weight [56], as defined below.

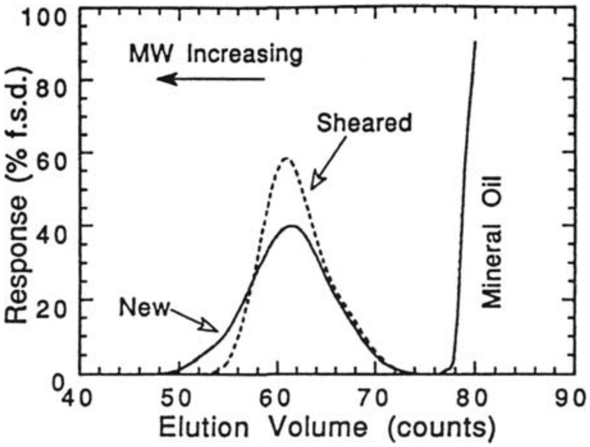
The higher the molecular weight, the more likely a polymer is to break. However, the mechanical degradation process is self-limiting, for at some point whatever the application, a molecular weight is reached where the energy concentration during coil distortion is insufficient to break further bonds, referred to as the limiting molecular weight. It should be noted, however, that molecules smaller than this will be produced since polymers only slightly larger than the limiting molecular weight still have a finite probability of breaking. Thus, the smallest molecule produced during shearing will be slightly greater than half of the limiting molecular weight. Viscosity loss during use is thus characterized by a rapid initial decrease as the bigger molecules break, followed by a slower loss and finally a plateau as the equilibrium, or terminal, molecular weight is reached.

Observations made by several workers using gel permeation chromatography, GPC, are entirely consistent with theory [57]. Figure 5.7 shows that only high molecular weight species are degraded and intermediate molecular weight polymer is produced, also that no low molecular weight fragments are made during mechanical shear. The kinetics of the degradation process has been modelled by numerous workers, but most tend to take the general form of that described previously [56], as in Equation (5.5):

$$\mathrm{d}B_\mathrm{i}/\mathrm{d}t = k(P_\mathrm{i} - P_\mathrm{c})n_\mathrm{i} \qquad \text{(Eqn. 5.5)}$$

where $\mathrm{d}B_\mathrm{i}/\mathrm{d}t$ is the rate of bond breakage of polymers with a degree of polymerization P_i, P_c is the limiting degree of polymerization for bond breakage, n_i is the number of molecules of size P, and k is a rate constant which is mainly a function of the shearing device but which may also be related to solvent and temperature. The total rate of bond breakage is summed over all molecular weight species big enough to shear degrade.

Fig. 5.7 Effect of VI improver mechanical shear on molecular weight, redrawn and adapted from [57]



It was proposed that there could be more than one shear zone for a given application, each with a different severity. Viscosity during shear would fit an expression containing two exponential decay curves, Equation (5.6), where *A, B,* C and *D* are constants for a given oil and application [58],

$$\eta = \eta_i - A(1 - 10^{-Bt}) - C(1 - 10^{-Dt}) \quad \text{(Eqn. 5.6)}$$

there could be more than one shear zone in a given application and that each could have a different severity, and this equation was shown to fit a wide variety of applications. Certain applications such as some hydraulic fluids and some automatic transmission fluids appeared to be satisfied by a single term, suggesting a single shear site. However, other fluids in the same device were best fitted by two terms, suggesting that different polymers can degrade by different mechanisms.

A somewhat different mechanism to that proposed by earlier workers still included multiple shearing zones and shear degradation in the FZG gear test rig was best fitted by a model using three shearing terms [59]. Shear degradation was observed to be a first-order process, suggesting that polymer entanglement was not a factor, also finding that the rate was proportional to the hydrodynamic volume of the VI improver and independent of the size and structure of side chain constituents [60, 61]. Thus, like thickening, shear stability is not a function of molecular weight across polymer classes but rather, to a first approximation, backbone length. An earlier observation noted that an OCP of 90,000 amu degraded to a similar extent as a PMA of ~200,000 amu [62].

Shear stability performance is generally expressed in terms of a scale referred to as the shear stability index, or SSI, defined as in Equation (5.7):

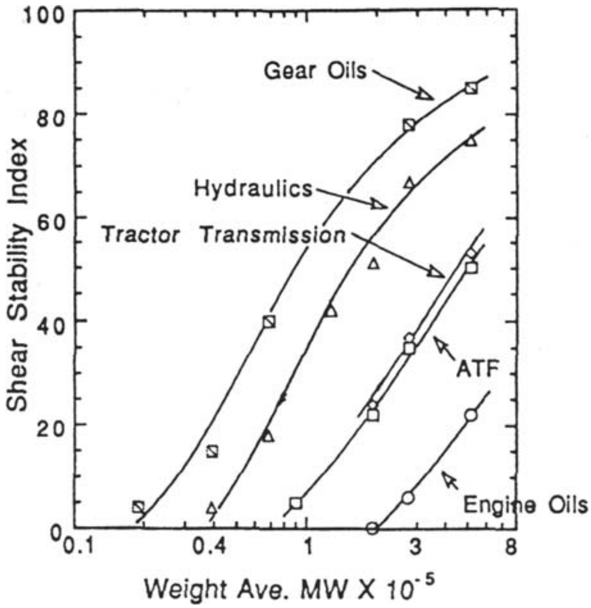
$$\text{SSI} = \frac{(\eta_i - \eta_f)}{(\eta_i - \eta_o)} \times 100 \quad \text{(Eqn. 5.7)}$$

where η_i is the initial formulated oil viscosity, η_f is the sheared oil viscosity, and η_o is the viscosity of the base oil including all additives except the VI improver. In practical terms, SSI is the percentage of the polymer-controlled viscosity which is lost as a result of shear degradation. The literature should be read with care since SSI can be misused or confused with overall viscosity loss, Equation (5.8). SSI is more useful, but it necessarily requires knowledge of the base oil viscosity, an unlikely situation when dealing with commercial lubricants.

$$\text{Overall viscosity loss} = \frac{\eta_\mathrm{i} - \eta_\mathrm{f}}{\eta_\mathrm{i}} \times 100 \qquad \text{(Eqn. 5.8)}$$

The severity of different lubricant applications covers a wide shear stability range. Figure 5.8 shows that engine oils are the mildest application, followed by automatic transmission fluids, hydraulic fluids and rear axle lubricants [63]. Thus, matching shear stability requirements of the application with the selection of VI improver is a key formulation consideration.

Fig. 5.8 Relationship of molecular weight to SSI for commoner VI Improver applications, redrawn and adapted from [63]



Extensive work has attempted to develop laboratory test methods which simulate viscosity loss in various applications, particularly engine oils in field service. Virtually any device which can shear polymers has been used, including sonic oscillators, ball mills, high-speed stirring, diesel injector rigs, pumps in hydraulic circuits, gear rigs, roller bearing devices and a variety of small engines, both motored and fired.

ASTM conducted a major program in the late 1960s to define the ultimate test. However, none of the candidate tests was completely satisfactory and it concluded

[64, 65] that the best way to measure shear stability for engine oils was to use an engine, a technique regarded as impractical because of the large sample requirement and high test cost. A small motored lawn mower engine was used to evaluate shear stability [66]; the technique is elegantly simple and, whilst it has not been widely used, it remains one of the best ways for relatively small-scale evaluation.

Whilst numerous bench tests are used in North America, diesel injector data are probably the most widely accepted. However, the Sequence VIII engine test procedure, formerly the L-38 engine test, is particularly important since it had been part of the heritage MIL-L-46152 (gasoline), MIL-L-2104 (diesel) and API requirements and is now included in the ILSAC GF series of specifications. Several bench tests are also important in defining European performance standards; their requirements are more demanding than those in North America mainly to meet the shear stability requirements of vehicles which have engines with integral gear boxes. This performance level was simulated by the Peugeot 204 viscosity stability test, CEC L-25-A-78. Since this vehicle configuration has been discontinued, the Peugeot test is no longer required in ACEA specifications, but this general performance level has been retained and is now measured using the Kurt Orbahn diesel injector test rig. A fair correlation was found between the two tests, but the Peugeot 204 was shown as being rather more severe [67]. API ‘C series’ heavy-duty engine oil specifications employ a 90 pass Kurt Orbahn D 7109-06 ‘Standard Test Method for Shear Stability of Polymer Containing Fluids Using a European Diesel Injector Apparatus at 30 and 90 Cycles’.

A spur gear test rig, the FZG test, has been used for many years and standardized as CEC L-37-T-85 and shown to be more severe than either of the other two tests described above [67]. This was confirmed in another study which also showed that a tapered roller bearing rig based on a modified four-ball apparatus, P-VW 1437, was still more severe than the FZG test [68]. These two tests have utility for the evaluation of gear oils and may also be of some value in severe hydraulic fluid applications. The TRB (tapered roller bearing) procedure, more commonly known by its German acronym, KRL, ‘Kugel Rollen Lager’ has been codified as CEC L45-T-93. It is widely used in gear oil applications and to a lesser degree in automotive and hydraulic fluid applications. Variations of the procedure involve duration of shearing with practices ranging from 4 hours to the very common 20 hours and in severe applications up to 192 hours. ASTM D 5621-01 ‘Standard Test Method for Sonic Shear Stability of Hydraulic Fluid’ is employed specifically in the classification of polymer-thickened multigrade fluids, according to ASTM D 6080-02 ‘Standard Practice for Defining the Viscosity Characteristics of Hydraulic Fluids’. Correlations for permanent viscosity loss for different fluids have been established using hydraulic fluid pumps of different mechanical types and different levels of pressurization [69].

In summary, there are numerous ways to simulate shear stability performance in operating equipment. However, a common thread in the literature is that all laboratory methods tend to have some degree of VI improver chemistry bias. They are generally valuable for evaluating a given chemical type, but they are not necessarily reliable in comparing different families of VI improver. Nevertheless, these tests can be extremely useful as long as the potential for bias is recognized. It must be stated, however, that there is never a total substitute for data from real equipment.

Temporary viscosity loss: All polymer solutions are non-Newtonian, that is, shear stress is not directly proportional to shear rate. There are several types of non-Newtonian behaviour, but VI improvers at high temperature exhibit only one; pseudoplasticity, or shear-thinning.

When an oil is subjected to shear stress, polymer molecules are distorted, as described above. The size, shape and alignment with the field of flow of these elongated structures are such that the polymer contributes less to viscosity than does the spherical, random coil configuration that exists at low shear stresses. The higher the shear stress, the lower the viscosity until a stable region, generally called the second Newtonian region is reached, Fig. 5.9. As long as the shear stress does not break the molecules, see Fig. 5.6, the process is completely reversible, i.e. when the shear stress is removed, the viscosity returns to its original value.

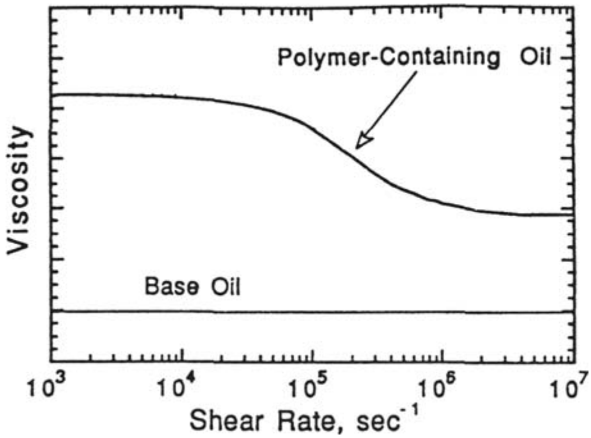
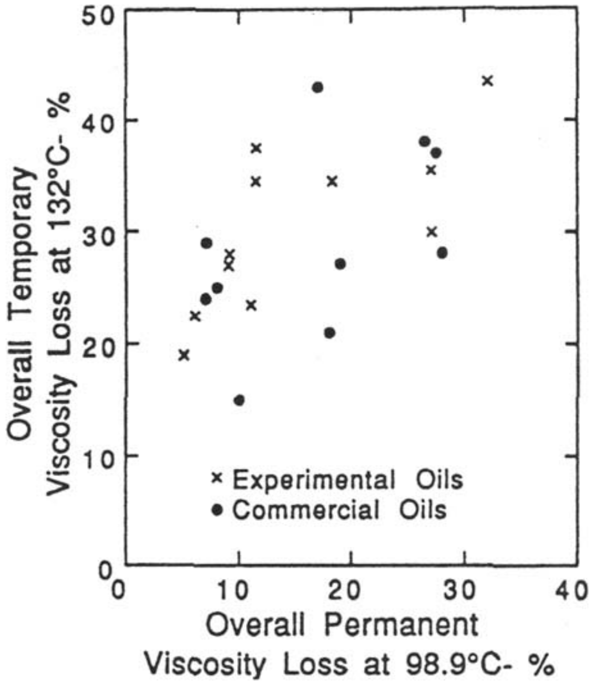


Fig. 5.9 Temporary shear stress

As with permanent viscosity loss, temporary viscosity loss is a function of molecular weight, thus the higher the molecular weight, the greater the temporary viscosity loss. It is also important to note that engine oils based on VI improvers which exhibit no permanent viscosity loss in service are still generally non-Newtonian, i.e. the molecules are distorted but there is insufficient energy to break chemical bonds.

There is no way to predict temporary viscosity loss across chemical families, or for that matter, sometimes even within chemical families. Examination of a wide variety of engine oils in a journal-bearing rig shows that there was no correlation between permanent and temporary viscosity losses; the same observation was made when measuring temporary viscosity loss using the flow rate through a journal bearing of a running engine [70, 71], Fig. 5.10.

Fig. 5.10 Temporary viscosity loss vs. permanent viscosity loss, after [71]



Primary polymer structure may account for some of the viscosity loss behaviour, but VI improvers which function as associative thickeners are a major confounding factor. When the physically associated multi-polymer structures enter a shear field, they can dissociate into their separate molecular species. These smaller individual polymers are low enough in molecular weight that they degrade either slowly or not at all. When the molecules leave the shear field, they associate again so that there is little or no permanent loss of viscosity. However, when in the shear field, the contribution to viscosity is from the smaller, distorted individual molecules. The net result is a system which exhibits a high temporary viscosity loss relative to its low permanent viscosity loss.

Coincident with the growing interest in high-shear-rate viscosity was the realization that the standard temperature for defining engine oil viscosity at high temperature, 100°C, is no longer representative of engine operation in the field. Thus, high-shear-rate viscosities and temporary viscosity losses are most often reported to 150°C whilst permanent viscosity losses normally continue to be determined at 100°C. The values at 150°C are typically called HTHS or HTHSR (high-temperature, high-shear-rate) viscosities.

Measurement of high-shear-rate viscosity of lubricants has advanced tremendously in recent years and is now relatively routine. High-pressure capillary and rotational viscometers are both commercially available, and both CEC and ASTM have defined standardized test methods for their use (CEC L-36-A-87, ASTM D 4683 and ASTM D 4741 for the rotational and ASTM D 4624 for the capillary).

The latter method is a generic one for a wide range of capillary viscometers. A separate method directed to a specific commercial high-pressure capillary viscometer is currently under development in ASTM Committee D.02, Subcommittee 7.

Combined permanent and temporary viscosity loss: Whilst much of the work that has been done in this area has focused on the isolated effects of permanent or temporary viscosity loss, equipment in the field obviously sees the combined effects. Limited work has been reported on the net effect, but effort in this area appears to be increasing.

A recent review of the literature on this subject has observed that changes in high-shear-rate viscosity at 150°C as a result of permanent viscosity loss was consistently small, relative to the change in low-shear-rate viscosity at 100°C [72]. In general it was found that the changes were half or less, but varied with the specific VI improver and other additive packages. However, considering the viscosity range of the current high-temperature viscosity grades relative to a comparable range for a system based on 150°C high-shear-rate viscosity, the HTHS change can be significant. As an example, a range of 2.9–3.6 cP at 150°C corresponds to a 100 VI extrapolation of the current SAE 30 limits at 100°C. The largest viscosity losses represented about 85% of the 100°C SAE 30 range but still 50% of the corresponding HTHS range. Thus, the changes in high-shear-rate viscosity with permanent shear are small on an absolute basis but significant on a relative scale.

5.4.4 Thermal–Oxidative Stability

VI improvers can also undergo a variety of thermal and oxidative reactions. The mechanical and thermal–oxidative processes differ in several ways, Table 5.2, and these processes may be important for several reasons. In the first place, backbone cleavage can lead to viscosity loss, much like the mechanical process. However, since chemical degradation is a totally random process, viscosity loss will only be important if breakage is well removed from the ends of the polymer. There are also deposit implications with the implication that oxidative breakage produces small, reactive fragments that could contribute to sludge formation [73]. This was demonstrated in the extreme when early workers explored the use of natural rubber as a VI improver, see Section 5.1. Finally, VI improvers themselves can also become part of a deposit, the most notable example being as part of diesel piston deposits. Degradation pathways can influence the magnitude of the VI improver contribution in such cases.

Table 5.2 Mechanical and thermal–oxidative processes of VI improvers

Mechanical	Thermal–oxidative
Molecular weight sensitive	Indiscriminate
Break near middle of molecule	Random break along chain
Self-limiting	Complete degradation possible
Insensitive to chemistry	Dependent on chemistry

In a sense, it is unfortunate that discussions of the chemical degradation of VI improvers combine thermal and oxidative effects since the two processes are quite different. A simple thermal process is one which can take place in the absence of oxygen and would include processes such as the random thermal scission of a polymer backbone, which may be followed by depolymerization. Another possibility for PMAs or SPEs is pyrolysis of the ester side chains to form olefin and acid. The acid, in turn, can react with an adjacent ester to form a cyclic anhydride with elimination of alcohol. Adjacent acid groups can eliminate water to make an anhydride [74]. There is no evidence that depolymerization and ester pyrolysis are issues in the engine oil itself, but they may be a factor if the VI improver is trapped in deposits.

The oxidative process is driven either by oxygen itself or by any source of free radicals. If a polymer backbone is attacked, leading to either a polymeric carbon or oxygen radical, backbone cleavage is possible. For polyethylene, polypropylene and butadiene- or isoprene-containing polymers, this may be accompanied by elimination of formaldehyde or acetaldehyde. For styrene-containing polymers, formaldehyde and benzaldehyde are products from the cleavage [74]. Such reactions could take place either in the bulk oil phase or in deposits in which the polymer is physically trapped.

Since oxidation is a chemical process, the established carbon–hydrogen bond strengths can be used to estimate ease of hydrogen abstraction, Table 5.3 [75]. These suggest that PMA backbones should be most stable to oxidative attack; OCP polymers would be expected to be less stable whilst the stability of styrene–diene polymers could vary depending on the extent of 1,2 vs. 1,4 structures present. The benzylic hydrogens from styrene are potential sites for attack, and it is obviously critical that hydrogenation of the olefinic unsaturation is as complete as possible.

Table 5.3 Carbon–hydrogen bond strengths of typical organic molecules [75]

Carbon atom centre	Carbon–hydrogen bond strength, D°_{298}, $kJmol^{-1}$
Primary	419.5 ± 4.0
Secondary	401.3 ± 2.0
Tertiary	390.2 ± 20
Benzylic	353.1 ± 6.3
Allylic	345.2 ± 5.4

The thermal and oxidative instability of major VI improvers was examined by determining the molecular weight distributions of samples subjected to several engine tests [76]. Given that the chemical pathways can lead to low molecular weight fragments while mechanical shear does not, it is possible to evaluate the importance of thermal–oxidative pathways in polymer degradation. PMAs exhibited only mechanical instability in a 40-hour test in an Opel Kadett engine, the Peugeot 204 test and the Caterpillar IH test with some thermal degradation only in the Caterpillar 1G test. In contrast, both OCP and HSD VI improvers showed very slight oxidative effects in the Opel Kadett and clear oxidation in all of the other tests. Furthermore, viscosity changes observed for the block HSD copolymer were larger than expected from the molecular weight change, leading to speculation that oxidation probably changed the polymer structure in a way that interfered with the associative thickening mechanism.

Thermal/oxidative effects contribute to viscosity change in the FZG test [77]. Diesel injector and FZG shear data were shown to correlate reasonably well in spite of evidence, based on GPC data, that the former appeared to be a purely mechanical process while the latter had a significant thermal and/or oxidation component. This may well relate back to the observation that a diesel injector shear process can best be simulated by assuming two steps [58], whilst others found that the FZG shear data appeared to involve three steps [59]. There is also a clear chemical bias indicating that the PMA thermal/oxidative component is less than that of other VI improvers in the study [77].

A study of oil solutions of PMA, OCP and HSD subjected to both thermal and oxidative processes found that there was no viscosity change at 170°C for any of the systems in the absence of oxygen [78]. However, in the presence of oxygen, the PMA solution lost very little viscosity while the OCP solution underwent severe degradation. However, at 260°C all systems degraded significantly. A separate study showed that this oxidative process could be decreased but not completely suppressed by antioxidant [79].

Overall, it appears that the thermal/oxidative behaviour of PMA VI improvers is dominated by thermal effects while that of the other current VI polymer improvers is dominated by oxidative effects. The trade-off between the two processes does not appear to be a dominant factor in choosing VI improvers.

5.5 Performance

5.5.1 Introduction

Preceding sections summarized the physical and chemical nature of VI improvers and the lubricants containing them; this section links those features to end-use performance properties. Since engine oils are by far the largest market for VI improvers, this application is the primary focus of this section.

There is no easy decision process for choosing a VI improver as any chemical family or shear stability option represents a compromise, in addition to overlying costs and convenience. It is sufficient to say that currently large quantities of all three major classes of VI improver are used in both gasoline and diesel engine oils. Whilst not discussed for the most part in following sections, a common thread to all performance areas is the role of new oil vs. used oil viscosities. Most work relates performance to new oil viscosities, since this is how industry viscosity standards are set at present. However, it is sometimes noted that relationships can be improved if sheared oil viscosities are used.

5.5.2 Low-Temperature Viscosity

Cranking: Polymer-modified engine oils give the benefit of low-temperature cranking as one of the primary driving force for commercialization of multigrade engine oils. Prior to using VI improvers, low-temperature properties were specified by extrapolation of viscosities at 210°F (98.9°C) and 100°F (37.8°C) to 0°F (–17.6°C) – the apparent precision of the (European) centigrade temperature standards arises from their conversion from the Fahrenheit (US) scale. The utility of this measurement was completely nullified by the non-Newtonian nature of polymer-containing oils. Instead the cold-cranking simulator, CCS, was adopted as the industry standard in SAE J300a in 1967, and developments in this area up to 1975 were carefully reviewed [80].

A study of the low temperature properties of several VI improver systems showed that at the high shear rate of the CCS, PMA, OCP and HSD (SBC) all had comparable viscosities. For the latter two, this results from substantial non-Newtonian character at low temperatures, Fig. 5.11 [81]. Results for polyisobutylene, PIB, adequately met the standards when extrapolated low-temperature viscosities were used.

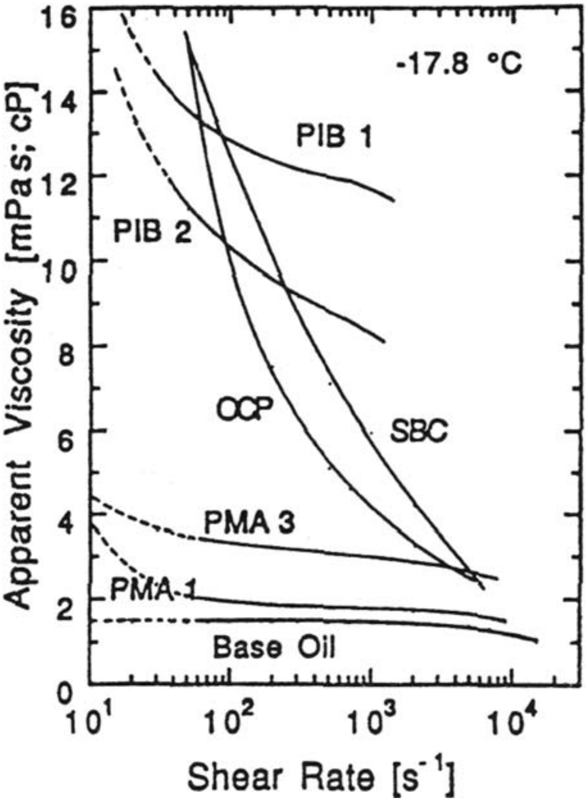


Fig. 5.11 Apparent viscosity vs. shear rate for various polymer types, after [84]

However, its measured viscosity at CCS shear rates is quite high, so that it could only be used with a very light base stock. This deficiency was the major factor which has led to its virtual disappearance from the engine oil market, of which until the mid-1960s PIB had a substantial share.

Data have been reported showing HSD VI improvers are reported to contribute less viscosity to the CCS than PMA or OCP, permitting the use of a heavier base stock [82], which had a favourable effect on base oil volatility reflected in improved oil consumption. Several reports demonstrated that dispersant PMA or OCP VI improvers in some cases permit a significant reduction in ashless dispersant level for fully formulated engine oils, also permitting use of a heavier base stock [17, 83].

The choice of shear stability level is also a major factor affecting the CCS viscosity, and therefore choice of base stock. Since shear stable, lower molecular weight, VI improvers are inherently poorer thickeners, high use levels are required with a necessary compensating reduction in base stock viscosity.

Pumpability: As a result of abnormally high wear during the winter months in the early 1960s, low-temperature pumpability requirements were introduced into SAE J300 in 1979. Unfortunately, the standards were flawed and severe field problems plagued the industry during the early 1980s. It was demonstrated that the severity of the problem varied greatly with engine design and that a major source of the problem could be caused by wax gelation or pour point reversion problems [85]. It was also shown that in the absence of wax problems, PMAs provided a superior performance to that of SIPs which, in turn, were superior to OCPs with the differences largest in the most severe engines [86]. This was confirmed with the additional observation that VI improver differences in performance were minimized for engines properly designed for low-temperature flow [87]. VI improvers' chemistry rankings were confirmed in a program which studied engine parameters further and included a broader range of SAE W-grades [88], supported by very similar observations for heavy-duty diesel engines [89, 90].

While differences in VI improver chemistry affect pumpability performance, it is emphasized that with good base stocks and proper choice of pour point depressant, engine oils can be formulated to industry standards with any of the currently used chemistries.

5.5.3 High-Temperature Viscosity

The high-temperature rheology of engine oils was the subject of extensive research and controversy during the 1980s as SAE and ASTM expended considerable energy to deal with the high-temperature part of SAE J300. The literature was thoroughly reviewed by an ASTM task force of Section D.02.07AB [91] and updated in a further review [92]. These investigations led to the inclusion of minimum HTHS viscosity limits in SAE J300 in 02/92 and revised in 03/93. The limits reflect a balance between lubrication and fuel economy needs, as explained below.

Journal bearing oil film thickness and wear: Lubricant issues related to journal bearings have been extensively studied using bearing rigs through oil film thickness measurements in running engines to catastrophic failure tests in full-scale vehicles. While it remains reasonably well established from the ASTM review [91] that high-temperature, high-shear-rate viscosity is an important parameter in determining oil film thickness, debate remains as to how important a contribution is made by pressure or viscoelastic effects. It was argued that the 150°C high-shear-rate viscosities of polymer-thickened oils measured at high pressure can be in a different order from that observed at atmospheric pressure [93]. A model lubricant based on very high molecular weight polyisobutylene demonstrated that elasticity can make an important contribution to journal-bearing load capacity [94].

Perhaps the most careful and thorough study of the subject by an ASTM task force in 1990 concluded that HTHS viscosity alone is sufficient to predict oil film thickness in running engines [95]. The key to reaching this conclusion was in establishing the oil temperature at the point of closest contact in the bearing, thus permitting the viscosity to be specified at the relevant temperature. The only VI improver chemistry issue involved is how associative thickeners fit into the total scheme.

Piston ring-cylinder wear: The piston ring-cylinder wall region of the engine is much more complex than bearings in that the lubrication regime is mixed, that is, hydrodynamic during piston travel and boundary at top and bottom dead centre. Furthermore, temperatures are higher than in the bearings, so much so that there could be a volatility issue overlaid on the rheology. The state of knowledge is included in the ASTM review [91] and is not covered here, it is sufficient to say that viscosity and VI improver effects were observed by several workers.

Fuel economy: It is widely accepted that there is a viscous component of engine oil fuel economy, extensively reviewed in the ASTM report [91]. There is general agreement that the viscous contribution is determined by high-shear-rate viscosities in the range of $4 - 10 \times 10^5 \mathrm{s}^{-1}$, measured at temperatures in the range 100–150°C and dependent on the vehicle service. It is also recognized that if the viscosity is too low, boundary effects will become important and fuel economy benefits will be lost. A secondary effect is the formulation practice dictated by the choice of VI improver chemistry. Fuel economy improvement is related to SAE W grade, with lower grades being more fuel efficacious because lower W grades require lower viscosity base oils and their attendant lower pressure–viscosity constants and lower traction coefficients. The VI improver chemistries allowing lighter base oils in any given SAE W grade would have an advantage to some degree.

Oil consumption: The role of lubricant formulation in oil consumption control has been studied sporadically for many years. There has been relatively little debate on the subject with nearly all workers concluding that there are both viscosity and volatility components. The only issue has been the relative contributions of the two factors, which not surprisingly vary with the nature of the formulation, the design of the vehicle and the severity of the service. Since the route of oil loss is behind the piston rings and down valve guides, the viscosity component is generally accepted as being low-shear viscosity. Hence, VI improver effects are correlated with kinematic viscosity (generally on the used oil) measured from 100 to 150°C, dependent on the service use. It was concluded that for current gasoline engine designs, volatility is the more important factor, although the relative contributions of viscosity and volatility vary with engine design, including whether the engine is air- or water-cooled [96].

The presence of VI improvers has a strong positive influence on oil consumption control in large diesel engines. The effect is not well understood, but it is clear that volatility is much less of a factor than in gasoline engines. In diesels, oil consumption is thought to result largely from oil pumped behind the rings and from a wave of oil carried upward on the top of the piston rings. When the piston reaches top dead centre, the oil is thrown by inertia into the combustion chamber. It has been speculated that it is the effect of polymer on the (low shear) viscosity behind the rings and in the wave of oil which is the favourable factor [97].

A description of using low levels of VI improvers in monograde oils to improve their oil consumption control properties noted that all VI improver chemistries in current use were effective [98]. It was argued that this effect is not the result of viscosity although no alternative was offered. The polymer concentration range described as being effective is similar to that described as being effective at controlling stray mist during mist lubrication [99].

A long-term lubricant effect on diesel engine oil consumption observed that oil consumption control is lost when carbon deposits build up on the top piston land [100]. VI improvers may be a factor in that they contribute to piston deposits, but their role in this specific phenomenon has not been demonstrated.

High-temperature pumping efficiency: High-temperature pumping efficiency is influenced by the role of viscosity in control of internal pump leakage, related to the high-shear-rate viscosity at test temperature [63]. It was also demonstrated that high-shear viscosity directly influences the pumping efficiency of hydraulic fluids as well as being a factor in gear upshifts in automatic transmissions [101]. Hydraulic pumping efficiency is also a factor in internal combustion engine operation particularly where hydraulic lifters are present.

5.5.4 Deposits: Diesel Piston Deposits

Early in the development of multigrade diesel engine oils, it was reported that the VI improver content in a formulation was a significant factor in contributing to piston deposits [102, 103]. Since it is generally accepted that all VI improvers contribute to these deposits, the importance of keeping the VI improver content as low as possible was emphasized. This gives OCPs a significant advantage over other chemistries, but there are also implications for shear stability level because of the higher polymer content required by a low molecular weight VI improver.

A carefully controlled experimental design using Caterpillar I-H2 tests observed no effect on piston top groove fill and only a very weak effect on weighted total demerits using two levels (differing by a factor of two) of dispersant OCP [104]. Additive packages must be customized to the VI improver chemistry for optimum performance [105].

Dispersancy: It has been pointed out that dispersant PMAs can replace a significant portion of the ashless dispersant necessary for sludge dispersancy performance in gasoline engines using either leaded or unleaded gasoline [83]. Significant varnish benefits were also noted by the use of dispersant or PMA VI improvers. Similar dispersancy performance was demonstrated for dispersant OCPs and also showed that the polymers can enhance performance in both gasoline and diesel engine oils [17]. Dispersant VIs can be used either to achieve higher performance levels or to displace ashless dispersant, allowing use of a heavier base stock.

Dispersant VI improvers and ashless dispersants are not necessarily a one-to-one trade-off. Both can be extremely effective in controlling sludge deposition in gasoline engines. As the very high dispersancy levels necessary for modern gasoline engine oils demand very high levels of ashless dispersant, corresponding light base oils would be necessary and dispersant VI improvers can be used advantageously for such cases. However, these trade-offs in diesel engines are more complex – ashless dispersants tend to be more effective in controlling diesel deposits, but dispersant VI improvers are better for dispersing soot in the oil. Dispersant VI improvers provided the best control of soot-induced viscosity increase with an inferred favourable effect on soot deposition in the engine [106]. Improved wear control was reported with these formulations which resulted from reduced abrasive wear.

Dispersant VI improvers cover a wide range of performance levels, related more to the nature of the dispersant functionality and its incorporation than to the chemical family of the molecular backbone. The generalizations described here are potential performance options to be evaluated for a particular dispersant VI improver of interest.

5.6 Prognosis for Future Developments

It is difficult to foresee any revolutionary changes in VI improvers in the future, recognizing that current core technologies in this area range from about 30 to 60 years old. The technologies in use are not that ‘old’ for all of them have undergone continuous evolutionary development change since their respective introductions. This development will continue driven more by adapting polymer technology than changing polymer technology, to meet the continually evolving needs of the lubricant market.

It is assumed that engines will continue to increase operating temperatures, placing continued pressure on the thermal–oxidative stability of VI improvers. Volatility will be an increasingly important issue for emissions-related objectives. VI improvers with minimum CCS contributions allow the use of heavier base stocks, desirable for volatility needs. However, volatility improvements conflict with fuel economy improvement since less viscous, more volatile, base oils are better suited. For highly fuel-efficient gasoline engine oils, VI improvers will have relatively high T-SSI (temporary SSI) to minimize viscosity in the high-temperature, high-shear-rate regime. For heavy-duty diesel engine oils where durability is of greater concern, VI improvers with lower T-SSI will be better suited.

Full synthetic and part-synthetic formulations will continue to grow, opening a market for VI improver products which are customized for these base stocks. As refining science produces more technically advanced base stocks, then VI improver chemistry must adapt to suit. As one example, gas-to-liquid, GTL, base stocks, as in Chapter 2, could appear in significant volume in the future. These base stocks have a VI of the order of 145 due to their highly paraffinic nature and will probably require VI improvers with some modified solubility characteristics as well as wax crystallization control, if this activity is to be provided by the VI improver.

Dispersancy may be a driver if higher levels are needed or if a different type of dispersancy is required. As gasoline and diesel engine lubricant formulation lines diverge, a parallel series of dispersant VI improvers could emerge, one optimized for low-temperature sludge dispersancy and the other for high-temperature deposit control and soot dispersancy. There is always the possibility of a different mode of dispersancy being needed as new engine technology produces new requirements, such as the example mentioned previously for soot in lubricants derived from heavy-duty diesel EGR cooled engines.

Products will need development and optimization for alcohol- and vegetable oil-based fuels. Evolution is likely to be both composition, to tolerate high levels of fuel dilution, and dispersancy to handle new types of sludge that are likely to be produced.

Low-temperature pumpability requirements may become more demanding, and evolution of all chemistries to improve this performance area should be expected. As the automotive and additive industries continue to become more aware of the low-temperature properties of used engine oils, dispersant VI improvers may be designed to prevent the thickening which now occurs at extended mileages. In summary, VI improver developments for the foreseeable future are likely to be evolutionary and market-driven.

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Chapter 6
Miscellaneous Additives and Vegetable Oils

J. Crawford, A. Psaila, and S.T. Orszulik

Abstract The need for friction modifiers in lubricant formulations is described. The chemical and physical aspects of friction modification are explained, with emphasis upon the structural contribution of adsorbed vegetable oil-based substances on metal surfaces. Applications of friction modifiers are discussed. The importance of determining a lubricant's pour point is described, and the action of certain structured compounds in decreasing pour point is explained. Demulsifiers and antifoams enable lubricants to separate entrained water and air in service use and prevent them from becoming emulsions and foams with very much decreased lubricity. Corrosion inhibitors are added to lubricants to prevent the acidic products of combustion resulting from fuel combustion, air entrainment and water condensation combining to corrode the internal metal components of engines. The chemical and physical properties of various vegetable oil structures are discussed in terms of their current and potentially future use in lubricant applications, as both base oils and additives.

6.1 Organic Friction Modifiers

6.1.1 Introduction

Organic friction modifiers or friction reducing additives have been established for several decades. Their original application was for gear oils, transmission fluids and slideway lubricants to eliminate 'stick-slip' effects from multipurpose tractor fluids for wet brakes and slideways, etc., anywhere where controlled movement is required. After the Gulf Crisis of 1978, fuel economy for all vehicles became an international issue, leading to the introduction of friction modifiers into automotive crankcase lubricants to improve fuel efficiency. Additional pressure was imposed in the United States on the oil and additive companies by the Corporate Average Fuel Economy (CAFE) regulations, a US government certification requirement for vehicle manufacturers. Reproducible measurements of fuel saving due to the lubricant became a target for the lubricant industry and led to development of the ASTM Sequence VI test for fuel consumption.

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To satisfy the Sequence VI requirements in the United States, the lubricant had to show decreased fuel consumption relative to a reference lubricant in a General Motors 3.8 l stationary test bed engine. From September 1995, this was replaced by the Sequence VIA test which uses a Ford 4.6 l engine in a similar manner although with a different test sequence. For lubricants claiming 'Fuel Efficiency' under the ILSAC GF-2 designation, the degree of improvement relative to a specified test lubricant is dependent on the starting viscosity of the lubricant. The engine test is relatively insensitive to friction modifiers and more sensitive to the lubricant viscosity. In Europe the Mercedes M 111 engine is used similarly, although it is more sensitive to friction modifiers.

6.1.2 Friction and Lubricating Regimes

Friction is defined as 'the resistance a body meets with in moving over another body in respect of transmitting motion'. The friction coefficient, μ, is defined as in Equation (6.1):

$$\mu = \frac{\text{Friction force}}{\text{Normal force}} \qquad \text{(Eqn. 6.1)}$$

An irregular rock dragged over an unlubricated irregular surface has a friction coefficient between 0.5 and 7. The coefficient of friction of dragging a flat stone over a flat rock is between 0.1 and 0.2. For a lubricated surface, the coefficient of friction is determined by the lubrication regime. In simple terms, there are two lubricant regimes: the hydrodynamic regime with a thick lubricant film and the boundary regime with a thin lubricant film, as in Fig. 6.1. Friction modifiers act most successfully in the boundary regime. The friction coefficient of hydrodynamic lubrication is between 0.001 and 0.01, which is effectively hydroplaning.

Friction coefficients determined via the pin-on-disc or the more modern technique of Cameron–Plint machine depend on the friction between two smooth surfaces. The typical surface roughness is about 10–15 μm, and such techniques investigate friction modification as a function of:

- pressure
- temperature
- surface finish
- surface material identity
- chemistry of the friction modifier.

Friction modifiers dissolved in oil are attracted to metal surfaces, and the resulting adsorption forces are very strong, as high as 60 kJ/mol. The polar head of

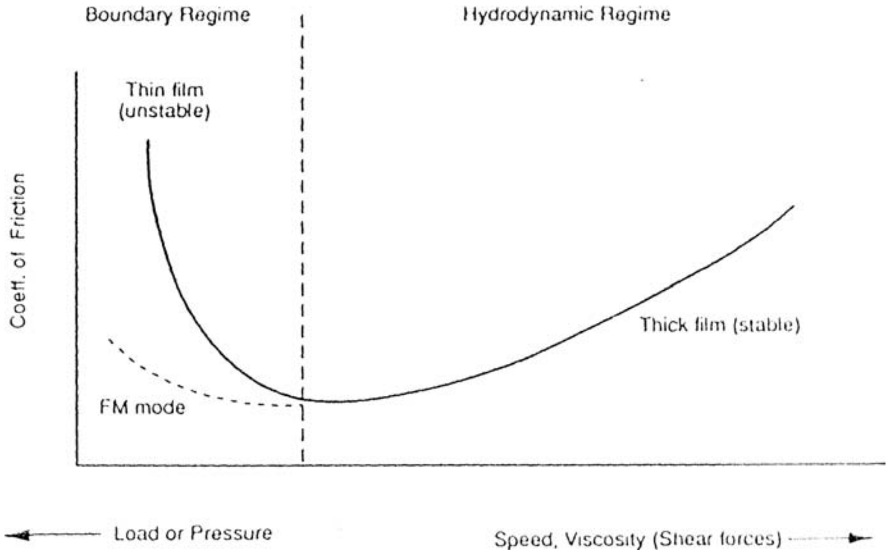


Fig. 6.1 Effect of viscosity, speed, friction modifier and load on friction and lubrication regime

the friction modifier is attracted to the metal surface, and the long hydrocarbon tail remains solubilised in the oil. The anchoring of the molecule to the metal surface results in the hydrocarbon tail being perpendicular to the surface. At normal concentrations, the friction modifier's hydrocarbon tails will align with each other and, through hydrogen bonding and Debye orientation forces, their polar groups can be attracted with a force up to 65 kJ/mol in dimer clusters, as in Fig. 6.2.

Van der Waals forces cause the molecules to align themselves such that they form multimolecular clusters parallel to each other. This orientation of the adsorbed layer can also induce further clusters to position themselves with their respective terminal methyl groups stacking onto the methyl groups of the adsorbed molecules being formed. This is similar behaviour to iron filings in a magnetic field aligning themselves along a particular force field. This double layer of molecules is hard to compress but very easy to shear, thus the slippery nature of the metal surface due to friction modifiers is readily appreciated.

The interactive forces between methylene carbon atoms and between methyl radicals are weak but positive estimates of <4–5 kJ/g have been made. Consequently, it can be seen that under normal stress conditions, such forces will lead to simple breaking and shear. On a molecular scale, it is easy to envisage that for two metal surfaces moving relative to each other, both surfaces would have the friction modifier adsorbed onto them.

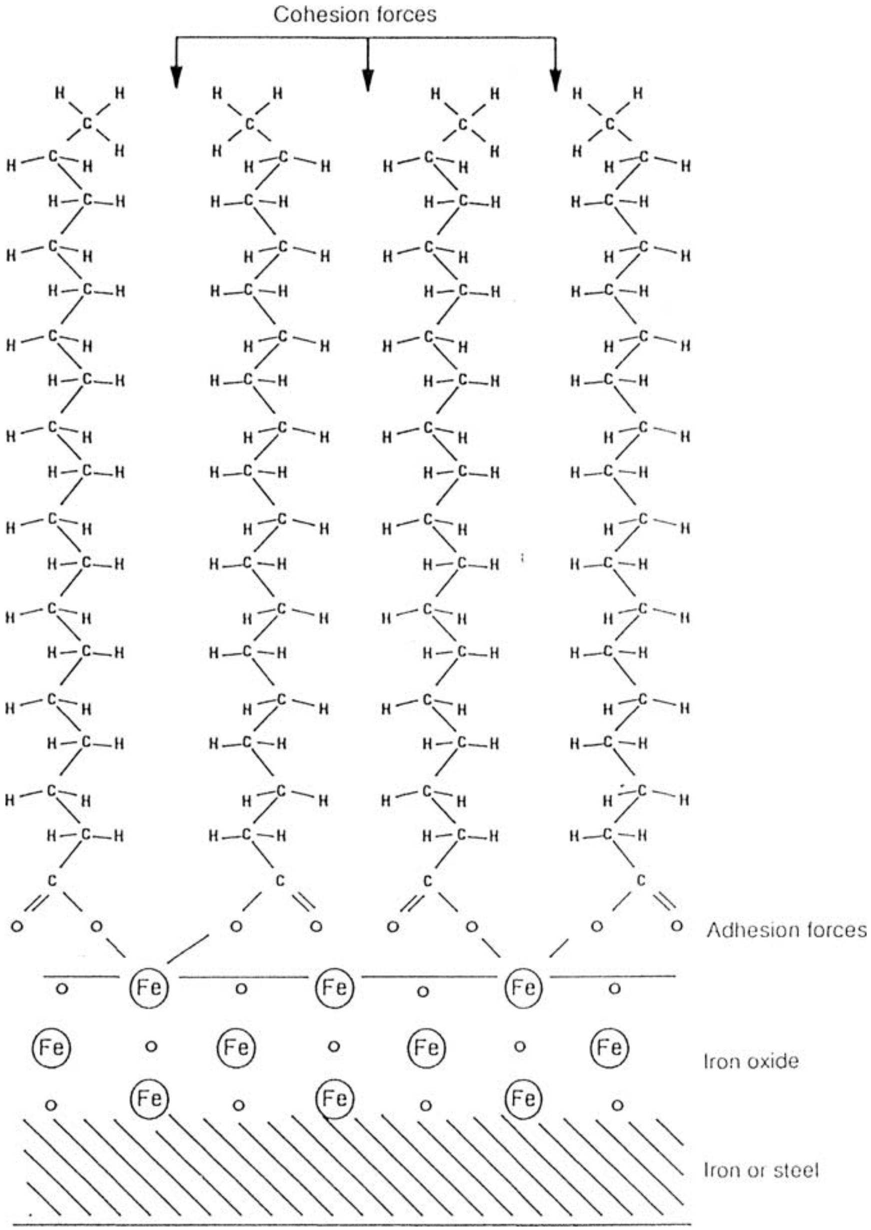


Fig. 6.2 Chemisorption of stearic acid onto an iron–iron oxide substrate

The stationary situation is shown in Fig. 6.3a. When force is applied to the adsorbed surface layers then they shear readily and appear in the oil, as in Fig. 6.3b.

A detailed structural representation is shown in Fig. 6.4.

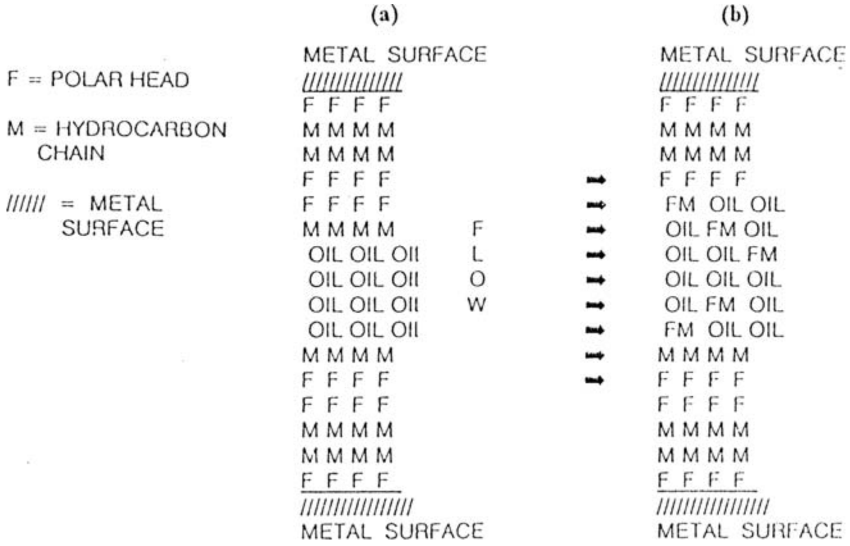


Fig. 6.3 Schematic illustration of the adsorption of friction modifiers (FMs) to metal surfaces: **(a)** stationary situation and **(b)** application of force leading to shear and appearance of friction modifiers in oil

6.1.3 Chemical Aspects of Friction Modifiers

As previously described, friction modifiers are usually long slender molecules with a straight hydrocarbon chain of at least ten carbon atoms. Hydrocarbons derived from natural products are ideal for such applications. The polar head group is the dominant factor in the effectiveness of the molecule as a friction modifier, such polar groups consist of:

- carboxylic acids or derivatives (including their salts)
- phosphoric or phosphonic acids and their derivatives
- amines, amides, imides and their derivatives

whereas alcohol and mercaptan polar groups are generally poor adsorbers in this situation.

A new type of calcium detergent chemistry has been described which has inbuilt friction modification [1]. Using an oscillating Cameron–Plint tribometer, this new class of additive lowers the friction coefficient of finished lubricating

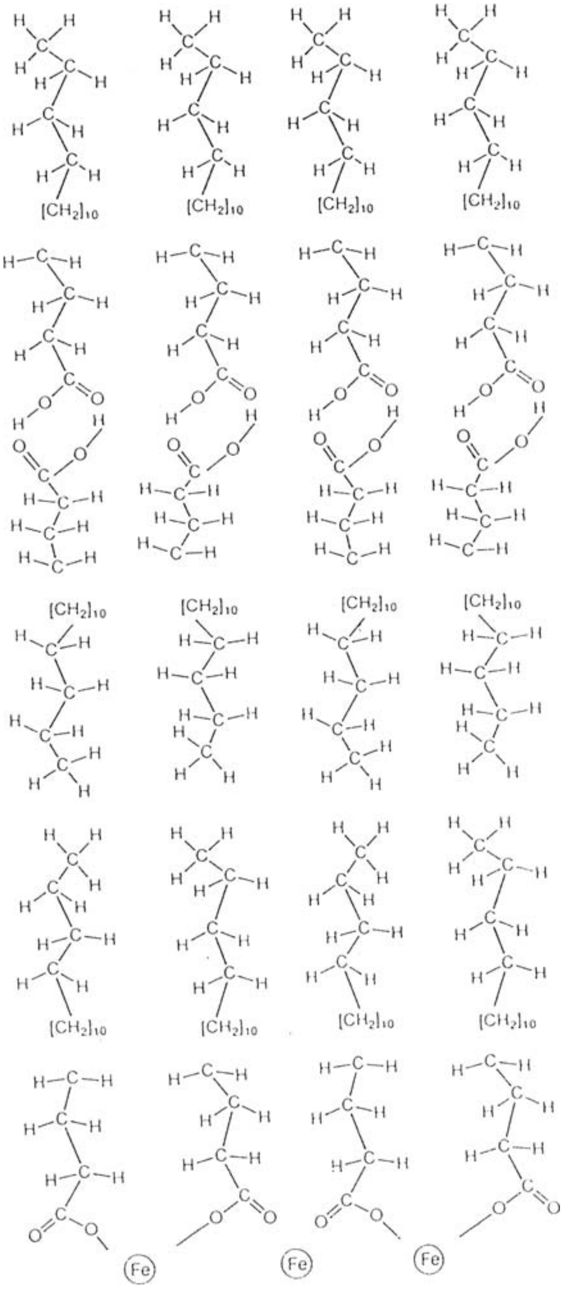


Fig. 6.4 Detailed structural representation of the adsorption of friction modifiers to metal

oils. Neutralisation of the calcium base by acid gives a decreasing friction coefficient. The long-chain natural acid present in these new calcium detergents is slowly released during neutralisation and migrates to the metal surface to form a friction-modified surface.

6.1.4 Antagonisms Between Friction Modifiers and Other Additives

Lubricant additives exert specific characteristics relative to the static and dynamic friction coefficients of a system. Figure 6.5 illustrates the effect of different additives at 1% treat rate on static and dynamic friction coefficients in a specific lubricating oil base stock. It can be seen from the plots in Fig. 6.5 that an incorrect balance of additives and friction modifier can alter the mechanism of movement in modern transmission systems such as the slideways of machine tools, wet brakes, automatic transmissions and limited slip axles. Incorrect combinations can adversely affect the performance and operation of the mechanism. Thus a high static coefficient combined with a low dynamic coefficient could cause gear movement problems together with squawk (noise) in automatic transmissions. If the static coefficient is too low then sliding and delayed gear engagement may result in loss of power. Major antagonisms can occur between friction modifiers and sulphur- and phosphorus-based EP additives. This can result in stick-slip motion in marine or machine tool slideways.

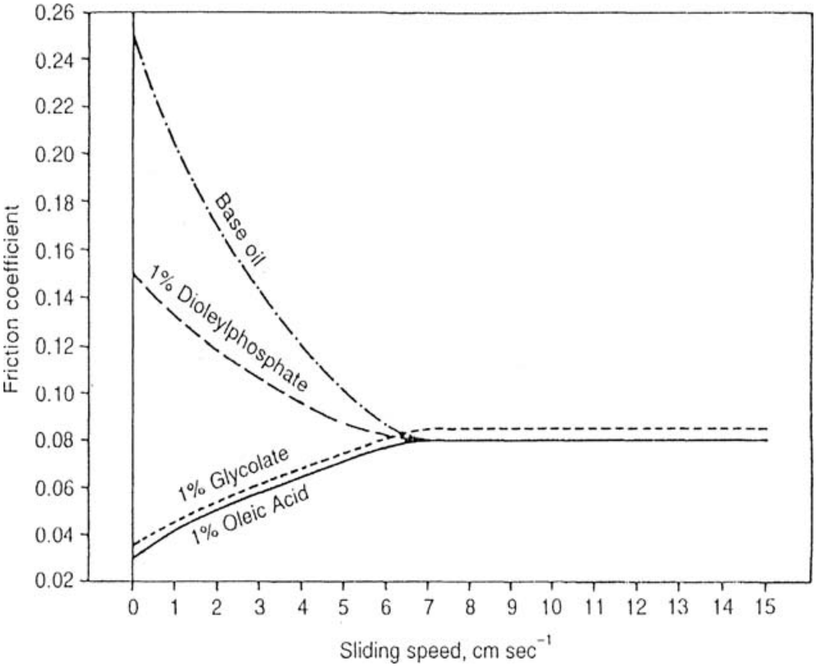


Fig. 6.5 Effect of different additives on static and dynamic friction coefficients

6.1.5 Lubricity Additives in Diesel Fuel

Diesel fuel fractions from the initial distillation of crude oil normally contain low levels of sulphur-containing heterocyclic hydrocarbons, see Chapter 1. Fifty/sixty years ago, the sulphur concentration in commercial diesel fuels could be 0.3, 0.5 or even 1%. Recognition of the environmental effects of the sulphur in diesel being released in urban areas as sulphur dioxide led to a staged, international reduction in diesel fuel sulphur. For developed countries, in 2008, the limit was 0.005%, or 50 ppm, with a target of 10 ppm around 2010 in the European Union. The problem is that whilst the naturally occurring sulphur-containing compounds in diesel fuel helped to lubricate the fuel pump, as the sulphur content of diesel decreased below 0.02%, it was found that diesel fuel pumps suffered catastrophic wear and failure. This wear is overcome by addition of small amounts of lubricity additives such as ethylene/vinyl acetate copolymers, effectively friction modifiers. The High Frequency Reciprocating Rig, ‘HFRR’, bench test simulates the wear effect of diesel fuel using a small ball-on-plate tribometer, and this is accepted by the fuel industry as CEC Test F06A/94.

6.2 Pour Point Depressants

6.2.1 Introduction

The pour point of a lubricant is determined by the ASTM D97 pour point test. In summary, the method records the temperature of the oil at 3°C above the point at which the oil will not move when tipped out of the horizontal.

The pour point test relates to the fluidity of a lubricant in an engine being very important under all circumstances. For starting up an engine from cold, it is important that the mechanical parts move freely because the lubricant is not too viscous. It is equally important that the lubricant is rapidly circulated to all parts of its circuit, known as ‘pumpability’ of the lubricant. Failure to do so will lead to excessive wear on cold starting with the engine subsequently becoming inefficient to the point of being inoperable. The main cause is generally lack of sufficient lubrication in the crucial, short, initial period of cold operation.

6.2.2 Low-Temperature Operation

When cooled to low temperatures, lubricating oil undergoes a number of changes, including (i) solidification, (ii) solidification with formation of a precipitate of macrocrystals of paraffin and (iii) solidification with the formation of microcrystals which swell to give a crystalline structure which traps the remaining oil. Collectively, these effects are called ‘waxing’.

When starting an engine from cold, it is important that the lubricant is not so viscous that the engine components are unable to move freely. Once the engine starts, it is equally important that the lubricant is rapidly circulated to all parts of the engine: this is referred to as the 'pumpability' of the lubricant. The circumstances under which waxing occurs are dependent on the thermal history, the cooling rate and the composition of the lubricating oil.

Naphthenic oils solidify forming an opaque solid phase and have naturally low pour points. Paraffinic oils of high normal paraffins tend to produce relatively strong structures made up of large (macro-) crystals. Isoparaffins give smaller (micro-) crystals of a weaker structure in a solidified oil. If the cooling rate is rapid, then crystal growth may be rapid and the oil will not remain fluid even on agitation. If a microcrystalline wax is formed, such deposits normally taking place at about 10°C, then the crystals can swell, behaving as a sponge with the absorption of free oil. This restricts the flow of the oil. Rapid cooling of an oil can produce a hard gel which is easily sheared. Motor oils generally use a mixture of different base oils and consequently exhibit a range of behaviours. Pour point depressant additives are used to improve the low-temperature characteristics.

6.2.3 Mechanism of Pour Point Depressants

Pour point depressants act through surface adsorption onto the emergent, growing, wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. In the absence of long interlocking crystals or swollen particles, oil can move freely through any solid wax particles that are present.

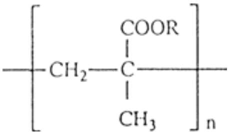
The limitations of pour point depressants are complex, controlled by the nature of the lubricant, the concentration and also the nature of the pour point depressant. The effect of pour point depressant varies widely with respect to the oil, but they are most effective with thinner oils such as SAE 10, SAE 20 and SAE 30 grades. Only small effects are seen with SAE 50 grade oils. Different types of pour point depressant also have different efficiencies, with the maximum effect occurring at an optimum concentration level. Above this optimum level, there is usually an appreciable effect on viscosity at higher temperatures. Typical levels of application in commercial oils are 0.1–1.0%.

In the severe winter of 1980–1981, problems with lubricating oil pumpability occurred. In the following winter, it was reported that, in addition to pumpability problems, oils would not flow out of containers. The problem was suspected to be the use of olefin copolymers, OCPs, which had a low level of crystallinity, with the result that when cooled or left overnight at very low temperatures, the lubricant gelled. With no lubricant in circulation via the oil pump and the oil distribution gallery, the camshaft sustained catastrophic wear. Special pour point depressants were developed to counteract these problems. This experience led to the development of the mini-rotary viscometer, MRV, and the associated test method, ASTM D3829. The mini-rotary viscometer predicts the low-temperature pumpability of an engine oil, and the test is incorporated into SAE J300 (SAE, 1989). The cooling curve for the MRV simulates the cooling of the oil in the sump when the engine is shut down at the test temperature.

6.2.4 Pour Point Depressant Additives

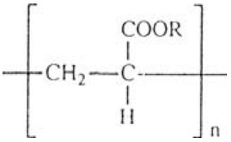
There are a range of pour point depressant additives of different chemical species:

(i) *Polymethacrylates:* represented by the unit group:

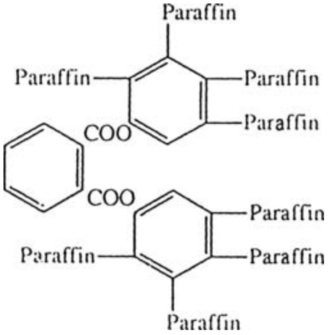


These are the most widely used pour point depressants. R in the ester has a major effect on the product and is usually represented by a normal paraffinic chain of at least 12 carbon atoms, which ensures oil solubility. The number average molecular weight of the polymer, M_n, is also very important; typically, these materials are between 7000 and 10,000 amu. Commercial materials normally contain mixed alkyl chains which can be branched.

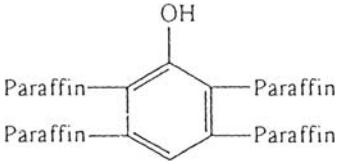
(ii) *Polyacrylates:* These are very similar in behaviour to the polymethacrylates



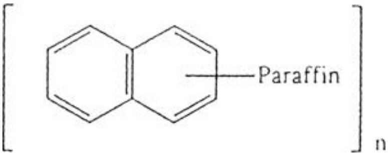
(iii) *Di(tetra paraffin phenol) phthalate:*



(iv) *Condensation products of tetra paraffin phenol:*



(v) *Condensation product of a chlorinated paraffin wax with naphthalene:*



6.3 Demulsifiers and Antifoams

6.3.1 Introduction

The normal operation of internal combustion engines subjects lubricants to considerable heating and mechanical shearing. In addition to the primary function of lubrication, therefore, lubricants must also deal with various combustion products, mainly acidic gases, moisture and carbon particles, which could harm the engine system. To deal with these contaminants, dispersant and detergent additives are incorporated into the lubricant formulation, see Chapter 7. These surfactants and other additives, such as viscosity index improvers, can have a stabilising effect on foams and emulsions that form under the high shear regime experienced in operating engines. Emulsions and foams can seriously impair the effective lubrication of an engine by starvation of the lubricant or by blockage of oil ducts. The lubricant and wear prevention effectiveness of lubricant foams is close to zero.

6.3.2 Emulsion Stabilisation

The presence of fortuitous water in the lubricant readily gives rise to the formation of water-in-oil emulsions stabilised by dispersant and detergent surfactants. Dispersants typically consist of a long hydrocarbon backbone, e.g. polyisobutene of molecular weight >900, and a succinimide head group formed by reaction with a polyamine such as tetraethylene-pentaamine. Detergents, on the other hand, consist of a calcium carbonate core surrounded by an alkyl-aryl sulphonate or a sulphurised alkyl-phenol shell. Clearly, either type of product is able to form strongly anchored interfacial layers which give a high degree of steric stabilisation to the emulsions. Other polar materials, e.g. soot and oxidation products, tend to accumulate at the interfaces. If the water droplets come into close proximity, they are kept apart by the repulsive interaction of the long oleophilic segment of the surfactants.

Positive crankcase ventilation and the recycling of blowby gases have, in some instances, resulted in the formation of a viscous emulsion sludge, especially in the colder parts of the engine. Lubricant formulation chemistry has to overcome this problem, but minimising the cold zones in an engine through better design is also important.

6.3.3 Demulsification

Demulsification can be usefully broken down into a series of stages. In the first instance, droplets must approach one another to form a loose aggregate. At this point, it is important to ‘sweep up’ small droplets before the next stage, coalescence, progresses too far. During coalescence, there is a dramatic reduction in interfacial area, resulting in the concentration of solids and other debris at the interface. These materials, which may have contributed to the stabilisation of the original emulsion, must be dealt with by dispersal into the bulk of one or other of the liquid phases. The formation of distinct phases can then be completed and the water removed.

The ease with which emulsions can be broken largely depends upon the ease with which the stabilising forces can be countered, and a combination of mechanical and chemical means is usually employed. Typically, demulsifier formulations comprise more than one component. To be effective, they must have limited solubility in the bulk phase, preferring to migrate to the interface, where they must be able to dislodge some of the stabilising surfactants. An important feature of demulsifiers is that they reduce the inter-droplet interaction which allows the droplets to come close together, forming an aggregation of droplets separated only by thin layers of oil. The rheological properties of this thin layer determine the ease with which it finally ruptures.

Mechanical aids to resolution of an emulsion are important. Although no chemical assistance is required to form a hard sediment of closely packed emulsion, stubborn emulsions require application of a chemical agent for the final film-rupture stage.

6.3.4 Demulsifiers

It is often said that the skill of formulating a demulsifier is a ‘black art’, selection of an effective product relying on a ‘trial and error’ approach, supplemented by the selector’s knowledge of what worked before. The test procedure requires the production of an emulsion under reproducible conditions. The rate of water coalescence is taken as a measure of the effectiveness of the product.

A wide range of products, including every class and type of surfactant, has been found to exhibit demulsification properties. The most commonly used products in lubricant formulations contain anionic surfactants such as alkyl-naphthalene sulphonates. Nonionic alkoxylated alkyl-phenol resins and block copolymers of ethylene oxide and propylene oxide are also used.

6.3.5 Foam Stability

The same surfactants that are responsible for the formation of stable emulsions almost certainly play an important role in the stabilisation of foams. Foams consist of a closely packed array of gaseous polyhedral cells separated by thin liquid films. The pressure differences across the films are similar; however, at the junction of the cells, curved regions of low pressure exist, called the Plateau borders, which form the causeway for drainage of the liquid. Gravitational liquid drainage is the prime mechanism of film rupture, directly related to bulk viscosity. The liquid film can be considered to consist of a sandwich of surfactant molecules at the gas/liquid boundary separated by a layer of the bulk fluid. Clearly a point will be reached at which the monomolecular surfactant layers come close enough to create a repulsive force which will delay film rupture.

Mechanical foam breakers and chemical methods are employed to destroy unwanted foams. The strategy is similar to that discussed previously for dealing with emulsions. The stabilising monomolecular surfactant must be sufficiently displaced to create a hole in the liquid layer. Antifoams are typically low-solubility surfactants.

6.3.6 Antifoams

The most important antifoam chemicals used to deal with non-aqueous foams are polydimethylsiloxanes. These are available in a range of molecular weights from low viscosity fluids of 1000 to several million cSt. Silicone fluids of the correct molecular weight have limited solubility in oil and a surface tension of 21 mN/m, lower than that of hydrocarbon oils. Fluorosilicones exhibit even lower surface tension, but their use is limited as they are considerably more expensive.

A variety of other materials including alkoxylated aliphatic acids, various polyethers, such as polyethylene glycols, branched polyvinylethers and polyalkoxyamines have been claimed to exhibit antifoam properties in lubricating oils.

6.3.7 Foam Studies

Characterisation of foams employs one of two techniques, either static or dynamic. In the static method, a foam is generated by sparging a gas into a liquid under controlled conditions and then stopped. The decay of the foam level is then monitored against time. The half-life of the foam is termed *the foam lifetime*. The dynamic method generates the foam continuously under standard conditions and the equilibrium volume measured. With care, a linear relationship between foam volume and gas velocity can be determined. The gradient of this linear response is the foam lifetime. It is not surprising that foam lifetime and viscosity show an identical dependence on temperature.

Traditional methods used for the study of foams employ one of three methods of generating a foam, namely single capillaries, sintered glass spargers and diffuser stones. Single capillaries give uniform bubbles but are relatively slow. The other methods generate a rapid foam with considerable turbulence, which adversely affects the reproducibility of the results. A turbulent-free foam can be created by using a uniform mesh to generate a foam of uniform bubble size. Direct measurements of single film thickness using optical methods can yield useful information on the critical film thickness.

6.4 Corrosion Inhibitors

6.4.1 Introduction

A corrosion inhibitor is defined (ISO 8044) as 'a chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agent'. This is a useful definition as it enables us to distinguish between the function of antioxidants and overbased detergents on the one hand and corrosion inhibitors on the other.

Antioxidants and detergents: In the course of its normal usage, a lubricant is susceptible to oxidation. The process of refining mineral oil strips the lubricant of its natural antioxidants (chiefly polycyclic aromatics and sulphur and nitrogen heterocyclics). Oxidation results in the formation of undesirable peroxides and acids. Antioxidants (e.g. hindered phenols and zinc dialkyldithiophosphates (ZDDPs)) are added to prevent the formation of these corrosive products. In addition, moisture and acidic combustion by-products enter the crankcase. To protect the engine from corrosive wear by mineral acid formed in this way, overbased detergents are incorporated in the lubricant.

Corrosion inhibitors: The conditions that influence the onset of corrosion are the entrainment of atmospheric oxygen, moisture from the combustion of fuel, and stop–start running coupled with temperature cycling. In the marine diesel engine, the problem is exacerbated by contamination with fortuitous saline. Corrosion inhibitors are added specifically to cope with this electrochemical process. These additives operate by creating a physical barrier, in the form of a dense hydrophobic, monolayer of chemisorbed surfactant molecules, which prevent access of the water and oxygen to the metal surface.

6.4.2 The Process of Corrosion

An electrochemical couple is formed between the ferrous metal and its oxide layer, invariably present. The anodic partial reaction generates electrons, Equation (6.2):

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^- \qquad \text{(Eqn. 6.2)}$$

In neutral or alkaline conditions prevalent in the lubricant environment, the corresponding cathodic partial reaction is Equation (6.3):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad \text{(Eqn. 6.3)}$$

Further oxidation results in the formation of hydrated ferric oxide or Fe(III) hydroxide, i.e. rust. The corrosion potential (E_C) and corrosion current (I_C) for the cathodic and anodic reaction can be represented by an Evans-type polarisation diagram, Fig. 6.6. Corrosion inhibitors interfere with the anodic or the cathodic partial reaction, or with both, resulting in a reduction in the corrosion current.

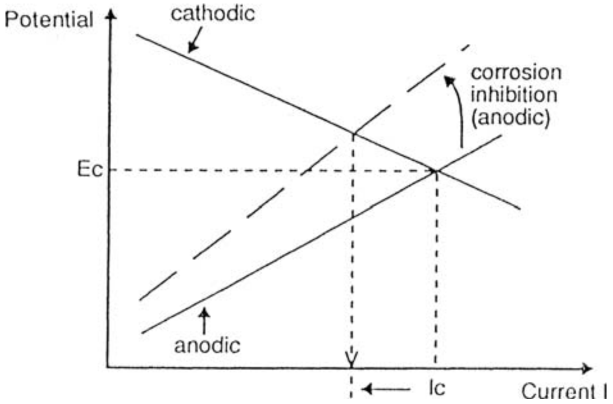
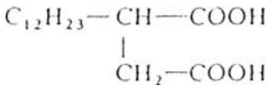


Fig. 6.6 Evans-type polarisation diagram

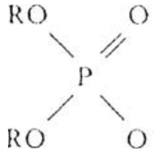
6.4.3 Corrosion Inhibitors

In the selection of an appropriate corrosion inhibitor, an important consideration is the problem of adverse competition with other additives designed to adsorb on the liquid–metal interface. Extreme pressure and/or antiwear agents compete for the same sites as the corrosion inhibitor. Fatty amines are good corrosion inhibitors in this type of environment. However, their adverse effect on the performance of ZDDP additives often prohibits their use. Half esters or amides of dodecylsuccinic acid, phosphate esters or thiophosphates are frequently employed. A combination of inhibitors is sometimes used, for example, fatty carboxylic acids or the dimer/trimer analogues of the unsaturated acids, e.g. oleic, used in conjunction with an amine such as an ethanolamine or alkyl amine, or amide such as alkyl imidazoline and sarcosines, Fig. 6.7. Shorter chain carboxylic acid and amines are used as volatile corrosion inhibitors.

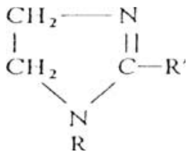


$$C_{12}H_{23}-\underset{\underset{\displaystyle CH_2-COOH}{|}}{CH}-COOH$$

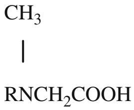
Dodecylsuccinic acid.



Phosphate esters (R = alkyl)



Alkyl imidazoline



$$R\overset{\overset{\displaystyle CH_3}{|}}{N}CH_2COOH$$

Sarcosines

Fig. 6.7 Examples of corrosion inhibitor compounds

6.4.4 Corrosion Testing

The ultimate evaluation of the corrosion protection afforded by a particular lubricant formulation is the Sequence IID engine test. This test simulates short trips in winter conditions. Such trips promote corrosion/rust on the engine components due to water condensation in the engine. The test lasts for 32 h, after which a rust rating is determined.

A variety of bench tests exist which attempt to evaluate the oxidative stability and/or the corrosion protection of a particular formulation. These invariably involve subjecting a coupon of one or more metals (chiefly copper and steel) to wet conditions for a fixed period at an elevated temperature. The assessment is carried out on the basis of weight loss and surface discolouration of the coupon.

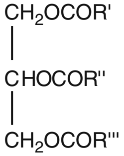
6.5 Vegetable Oils

6.5.1 Introduction

Fats and oils derived from animal and vegetable sources, generally known as lipids, have a long history of use as lubricants. Indeed, they were the main source of lubricants before the enormous growth of mineral oil-based products during the first half of the 20th century. Modern lubricants are predominantly based on mineral oil due to price and overall performance, although there is a continuing use of vegetable oils in lubrication. There is also an increased interest in expanding the use of vegetable oils in many lubricant applications, driven mostly by environmental concerns and legislation. Furthermore, vegetable oils are feedstocks for the oleochemical industry to produce a wide variety of chemical materials which are used in many applications, including lubricants, either as additives or for the production of synthetic materials such as ester base fluids.

6.5.2 Chemical and Physical Properties

Most vegetable oils (and animal fats and oils) have the triglyceride structure, Fig. 6.8, as tri-esters derived from glycerol and fatty, carboxylic, acids. The fatty acids are almost always straight chains containing between 8 and 22 carbon atoms and may be saturated, mono- or polyunsaturated. Vegetable oil compositions are normally described in terms of their fatty acid content, referring to the acid ester moieties; actual fatty acids present in the oil are known as free fatty acids.



$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOR'' \\ | \\ CH_2OCOR''' \end{array}$$

Fig. 6.8 Triglyceride structures

Each vegetable oil is characterised by its fatty acid composition which nevertheless may vary somewhat depending upon factors such as weather, soil conditions and variety. Typical fatty acid compositions of the most common vegetable oils, which together account for over 90% of world production, are given in Table 6.1 In the table, both non-systematic names and numerical notation are given, as an example, 18:2 refers to a fatty acid with 18 carbons and two double bonds.

Naturally occurring fatty acid components of vegetable oils virtually always contain an even number of carbons. In nature, the fatty acids in triglycerides display positional isomerism; they are not randomly distributed among the three possible positions of glycerol. For instance, palmitic acid in both olive and soya oils is present predominantly on the 1- and 3-positions rather than the central, 2-, position of glycerol. The double bonds are in the *cis* configuration and, in the case of polyunsaturates, are normally separated by a methylene group, i.e. they are not conjugated. For instance, the structure of linoleic acid, a common 18:2 acid, is given as in Fig. 6.9.

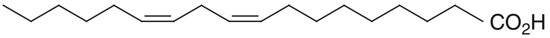


Fig. 6.9 Structure of linoleic acid

Table 6.1 Typical fatty acid composition of some common vegetable oils

Non-systematic name and numerical representation		Typical % fatty acid composition									
										Rape	
		Soya	Sunflower	Olive	Peanut	Cotton	Palm	Palm kernel	Coconut	High Erucic	Low Erucic
		(34.8)*	(10.5)	(2.7)	(4.5)	(4.9)	(35.2)	(4.1)	(3.3)	(17.7)	
Caprylic	8:0							3	8		
CAPRIC	10:0							4	7		
Lauric	12:0							45	48		
Myristic	14:0					1	1	18	16		
Palmitic	16:0	11	6.5	14	10	22	45	9	9	2	4
Palmitoleic	16:1					1					
Stearic	18:0	3.5	4	2	3	3	4.5	3	2	1	1
Oleic	18:1	22	21.5	64	42	19	38	15	7	15	60
Linoleic	18:2	54	66	16	38	53	10	2	2	15	20
Linolenic	18:3	8								7	9
Arachidic	20:0				1.5						
Gadoleic	20:1				1					7	2
Behenic	22:0				3						
Erucic	22:1									50	2

*Values in parentheses are world annual production, Mt/pa [2]

Differences in the physical and chemical properties of vegetable oils are largely dependent on the degree of unsaturation of the constituent fatty acids. Vegetable oils with a high proportion of saturated fatty acids are solid/semi-solid at room temperature and are generally referred to as 'fats'. The distinction between fats and oils is simply whether they are solid at room temperature. In nature, most fats are derived from animal sources, whereas lipids from vegetable sources are usually oils.

The presence of a double bond, or bonds, gives a kink in the chains which, particularly due to the *cis* configuration, are not able to pack together as readily as saturated chains. This gives a lower melting point with a consequence that unsaturated vegetable oils are mainly liquid and free of waxy deposits at room temperature. However, the presence of double bonds has an important effect on oxidative stability. The hydrogen in an allylic position is labile and hence susceptible to free-radical abstraction and subsequent formation of peroxides. In polyunsaturates, the methylene group separating double bonds is doubly allylic and therefore particularly prone to oxidation. The 'drying oils' use this process which ultimately leads to solid gels through the formation of a crosslinked network.

Hence lubricants based on vegetable oils for applications where both low-temperature performance and oxidative stability are required are probably best served by using an oil high in monounsaturates. This seeks a compromise between low-temperature performance and oxidative stability, with appropriate additives being used to improve performance where required.

As most vegetable oils are tri-esters, they are prone to hydrolysis which may cause problems for some applications. A small degree of hydrolysis may be acceptable, or even beneficial, since free fatty acids produced from hydrolysis are generally active as friction modifiers. Flash points of vegetable oils are very high, generally above 300°C, but this can be significantly affected by the presence of free fatty acids. The fairly consistent molecular weights and molecular interactions of vegetable oils give fluids which are viscous with a very high viscosity index, for example, the VI of rapeseed oil is over 200 [3].

The use of castor oil in lubricants is particularly important, both historically and currently. Castor oil is a triglyceride with a very high, ~90%, content of the fatty acid, ricinoleic acid, an unusual fatty acid, containing one double bond and a hydroxyl group, as in Fig. 6.10.

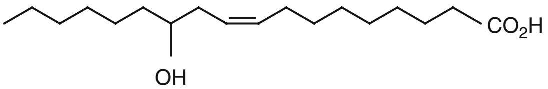


Fig. 6.10 Ricinoleic acid

The free hydroxyl group in ricinoleic acid is able to interact with polar groups on metal surfaces, thereby giving superior lubricity. The largely mono-ene nature of castor oil gives it low-temperature fluidity without the loss of oxidative stability of polyunsaturates. Castor oil is used in specialist two-stroke applications and can be modified for use in greases.

Another oil of interest for lubricants is jojoba oil as a replacement of sperm whale oil, the use of which is now banned. Jojoba oil is not a triglyceride but is a wax ester composed mainly of straight chain esters of C_{20}–C_{22} monounsaturated acids and alcohols. The major constituents, shown in Fig. 6.11, are eicosenyl and docosenyl eicosenoates, where $m = 9$ and $n = 10, 12$:

Fig. 6.11 Main constituents of jojoba oil

$$CH_3(CH_2)_7CH=CH(CH_2)_mCO_2(CH_2)_nCH=CH(CH_2)_7CH_3$$

$$m=9;\ n=10{,}12$$

6.5.3 Extraction and Processing

In nature, vegetable oils are generally concentrated in the seeds and fruits of plants. After harvesting, the vegetable produce needs to be transported and stored, factors which have an important influence on oil quality and quantity. Unlike mineral oil, the seeds or fruits can be affected by natural processes such as attack by insects, moulds and bacteria. Oil-bearing fruits such as oil palm and olive have a high moisture content which favours the action of naturally occurring enzymes. Hence these fruits must be processed soon after harvesting, whereas seeds, on the other hand, have a lower moisture content and may be stored for much longer periods. Before extraction, the raw material is often processed to aid the extraction stage [2], which may consist of some of the following:

- cleaning,
- dehulling or decorticating,
- cooking to break down the oil cells, sterilisation and coagulation of the protein,
- flaking.

Oil is extracted from the vegetable raw material usually by one of the following processes:

- screw pressing,
- pre-pressing, followed by solvent extraction,
- solvent extraction alone.

Process choice depends very much on raw material type and required plant capacity; continuous solvent extraction is often the method of choice for high throughput. Direct solvent extraction is particularly used for seeds that are low in oil, such as soya.

In screw processing, the oil is expelled under pressure exerted by a revolving worm shaft. High pressures can be achieved, yielding a cake with only 3–6% oil content. In pre-pressing, the pressures are about half those used in high-pressure expelling and the capacities are generally much higher. Oil is obtained in the pre-

pressing operation, though the main objective of pre-pressing is to obtain a cake suitable for the subsequent solvent extraction.

Solvent extraction, whether direct or following pre-pressing, is performed either by a percolation-type method or by immersion, in which the pre-treated seed or cake is dispersed in the solvent. Both methods employ a counter-current technique, and the degree of extraction is controlled since relatively high levels of impurities may be extracted towards the end of the procedure. The most widely used solvent is a light paraffinic petroleum fraction, which is recovered by passing through a multistage rising film evaporator.

Finally, the oil undergoes a number of refining processes to produce a purified oil. These refining processes may include degumming, in which phospholipids are removed as gums in a hydration process; neutralisation and washing to remove free fatty acids, trace metals and other water solubles; oxidation and deodorisation to remove by-products; and polishing to remove trace oil insolubles.

6.5.4 Uses of Vegetable Oils

As noted previously, vegetable oils have a long and continuing history of use in lubricants, though modern lubricants are predominantly based on mineral oils due to cost and performance considerations. However, recently there has been increased interest in extending the use of vegetable oils in lubricants driven mostly by environmental, as well as health and safety issues, and also arising from changes in economic and supply factors. There is a plentiful supply of vegetable oils in many parts of the world where mineral oil is expensive and in short supply. There is growing concern about polycyclic aromatics, PAHs, present in mineral oils posing a risk to human health, particularly in circumstances where, as a result of normal use, there can be considerable skin contact with the oil. Vegetable oils are free of PAHs and low in potential pollutants such as sulphur-containing compounds. They also have added advantages as environmental concerns grow in that they are biodegradable and are a renewable resource.

Unmodified vegetable oils have a number of applications in modern lubricants, both as additives and as general base fluids [4, 5]. As examples, high-erucic acid rapeseed oil has been shown to be effective in lubricants, and jojoba oil is used in high-performance automatic transmission fluids as a replacement for sperm whale oil, after the sperm whale was placed on the endangered species list in 1972. Vegetable oils may also be used as base fluids for straight cutting oils [3]. Reference has already been made to the use of castor oil in lubricants, particularly in two-stroke engine applications, where it is used essentially as a lubricity additive and is known for giving a characteristic exhaust odour.

Vegetable oils have several performance advantages over mineral oils. In general, they have superior lubricity, higher flash points and higher viscosity indices, which means their viscosity varies less with changes in temperature [6]. Their main disadvantages are related to their performance at both low and high temperatures. At low temperatures, vegetable oils start to solidify more readily than mineral oils as the straight chains within the vegetable oils align themselves and begin to crystallise. The presence of double bonds in unsaturated vegetable oils improves low-temperature performance as the chains are less able to align themselves. But double bonds make the molecules vulnerable to oxidation and thus their high-temperature oxidative stability can be poor.

In the past, the performance of vegetable oils was usually investigated using additive packages developed for mineral oils, which often gave poor performance. This left vegetable-derived lubricants with a reputation of poor performance. This was not always valid in that the performance of vegetable oils can often be better enhanced using additives specifically developed for this purpose rather than just using the equivalent package as used with mineral oil base stocks. Additives are now available aimed at improving the performance of vegetable oils for specific applications, such as antiwear hydraulic fluids, food machinery oils, marine two-stroke oils and chain bar lubricants [6]. Some applications are total loss systems, such as in two-stroke engines and chain bar lubrication. In total loss systems, the used lubricant is expelled directly into the environment where it may cause immediate damage, and hence there is an added incentive to use more environmentally acceptable lubricants such as those based on vegetable oils.

Rapeseed oil has been used in Europe for some environmentally sensitive applications, partly driven by regulations in some European areas, USB 2006 in [6]. Though generally the regulatory pressure is weaker in the United States, regulations are likely to arise more at the state level rather than the federal level. Furthermore, US Executive Order 13101 encourages federal agencies to use biobased products and will add to this pressure. In the United States it is likely that, due to price and availability, soya-based lubricants will play an increasingly larger role in lubrication, USB, 2006 [6].

Vegetable oils are used as raw materials for the oleochemical industry which supplies a vast range of materials [7]. Some of these largely retain their original triglyceride structure, whereas others are broken down and modified, perhaps with the addition of petrochemical materials. In this way, various alcohols and acids of vegetable origin are used in the manufacture of esters for use in synthetic ester lubricants. Most modifications, initially at least, are concerned with reactions involving the ester or double bond of vegetable oils. Hydrolysis gives the free fatty acids which are generally active as friction modifiers. Transesterification results in fatty acid esters which, in the case of rapeseed methyl ester, has been shown to be potential substitutes for diesel oil as ‘Fatty Acid Methyl Ester’, or FAME.

Soaps of 12-hydroxystearate, derived from castor oil, have superb thickening and lubricity properties and are hence used in greases. Sulphated castor oil is used in a mineral-based lubricant for pre-sizing polyester fibres and thus minimising abrasion. Ethoxlyated castor oil is a hydrophilic emulsifier which has found use in metal-working fluids.

The pressure for increased use of vegetable oils in lubricants, due to environmental as well as health and safety considerations, is likely to continue. New genetic varieties, commercialisation of existing varieties, together with new chemical modifications will increase the types of materials available. Economic trends are likely to make vegetable oils increasingly more attractive than in the past in many global areas. All these factors will probably result in the increased use of vegetable oils in lubricants, a trend evidenced by the number of patents and other publications in this area. However, the predominant position of mineral oils as base fluids is likely to continue for the foreseeable future; in terms of possible production volumes, vegetable oil surpluses could only ever replace a small share of the total mineral oil-based lubricant market.

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Chapter 7
Detergents and Dispersants

E.J. Seddon, C.L. Friend, and J.P. Roski

Abstract Lubricant detergents are metal salts of organic surfactants giving corrosion protection, deposit prevention and other formulation performance enhancements. Overbased detergents incorporate colloidal basic inorganic components which neutralize acidic contaminants. Degrees of overbasing, size and form of component affect detergent performance. Sulphonate-, phenate- and salicylate-type detergents incorporating calcium carbonate are the most widely used. Choices of detergent type and level are highly dependent on specific applications, and combinations are needed to optimize performance and cost.

Dispersants stabilize contaminants during a lubricant's lifetime and ameliorate negative effects of viscosity increase, wear, filter plugging, etc. Dispersants contain polar head groups with non-polar side chains with a range of molecule types available, reflecting formulation needs for many applications of different performance. Enhanced future lubricant specifications and new engine hardware require development of innovative dispersant technologies.

7.1 Introduction

The primary function of a lubricant is to create a film barrier between moving mechanical parts to reduce friction and wear. It also acts as a coolant, suppresses harmful deposit formation and controls corrosion/oxidation. Since the base oil alone would struggle to meet these challenging demands, performance-enhancing additives in tailor-made formulations are added to the lubricant formulation. These packages can include antioxidant, antiwear, corrosion inhibiter, viscosity modifier, detergent and dispersant components. Not only do these additives improve overall efficiency in the engine, but they also extend the lifetime of the lubricant.

Of these additives, the main purpose of the detergent and dispersant is to maintain cleanliness within the lubricant. This ranges from reducing carbonaceous deposits from hot metal surfaces to inhibiting dirt agglomeration via the formation of stable micelles. The basic nature of these components also serves to neutralize acidic components generated during oil aging, thus reducing corrosion. The general utility of these additives means they are now utilized in the majority of automotive

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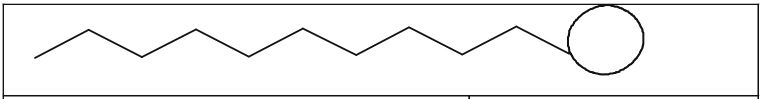
applications. For example, gasoline and diesel fuels are top-treated with ashless dispersants to keep fuel injector and inlet valves clean from deposits.

To satisfy the specific needs of these applications, numerous detergent and dispersant substrates have been developed. The aim of this chapter is to highlight the synthesis and utility of the most industrially important of these. Emphasis will be given to engine lubricants since this application has the largest commercial demand for detergents and dispersants. But other key areas, such as gear oils, transmission fluids and fuels, are also considered.

7.2 Detergents

7.2.1 Introduction to Detergents

Detergents have been used in engine oil applications since the 1940s. Originally, neutral metal salts of long-chain organic acids, typically alkylaromatic sulphonates, were used in engine lubricants to reduce the formation of carbonaceous deposits on the hot surfaces of engine parts such as piston ring grooves, Fig. 7.1. As a result of their cleaning ability and chemical similarity to aqueous detergents, such as those used in laundry soaps, these lubricant additives came to be known as 'detergents'.



Hydrocarbon tail	Polar head
Hydrophobic	Hydrophilic
Provides oil solubility	Metal attachment point

Fig. 7.1 Detergent substrate

'Overbasing' of detergents advanced the performance contribution of these materials as lubricant additives. Overbasing involves incorporating additional base reserve into the original neutral detergent structure, usually in the form of a colloidally dispersed metal carbonate such as $CaCO_3$. In their simplest form, overbased detergents can be considered as a mixture of the neutral metal salt of the organic surfactant with metal carbonate. Overbased detergents impart basicity to the oil to neutralize acids formed during the combustion process and from the degradation of the lubricant. They can also impart other performance benefits to the lubricant, such as antiwear [1] and antioxidancy or serve to act as rust and corrosion inhibitors [2].

As stated above, the term detergent implies that these additives impart a cleaning action to the lubricant. The detergent soap, or surfactant, acts in two ways: either by suspending particulates and deposit precursors in the oil to inhibit deposit formation or by coating the metal surface to form a barrier that hinders deposit formation. Although the details of the mechanism are not completely understood [3], they differ somewhat from ionic or non-ionic cleansing agents used in aqueous applications.

Over the years, detergents have found equally important usage in many other types of lubricants, including gear oils, farm tractor hydraulic fluids, automatic transmission fluids and industrial oils. The performance properties that detergents impart to these lubricating fluids include rust and corrosion prevention, improvement in lubricant elastomeric seal compatibility, enhancement of sludge control under oxidative conditions and improvement of wet clutch and wet brake friction level and stability.

A large variety of chemical structures that can be classified as detergents have been used in lubricants. In this section, we will review the basics of the most common detergent structures and the chemistry of their production.

7.2.2 The Fundamentals of Detergent Composition

Detergents are composed of an oil-soluble portion, called the substrate, and a metallic-counterion portion. The chemical structure of the substrate may vary considerably; however, it is typically an organic acid attached to a hydrocarbon chain. The common substrates in commercial use today include, in relative order of importance:

- sulphonic acids
- alkylphenol/alkylphenol sulphides/formaldehyde-coupled alkylphenols
- carboxylic and salicylic acids

Each of these substrates will be separately discussed in later sections.

Detergents can also be prepared from other organic substrates, such as alcohols, mercaptans, amines and alkyl-phosphonic or -thiophosphonic acids, but these are much less commercially significant than the three main types mentioned above.

A variety of metallic counterions can be combined with the organic surfactant to form the detergents. The three most commonly used today are calcium, magnesium and sodium. Other counterions that can be used include barium, lithium, potassium, aluminium, zinc, lead and strontium; however, these are much less common.

7.2.3 General Chemistry

The fundamental chemical reaction used to prepare a simple detergent is shown as Reaction (7.1):

$$\begin{array}{ccccccc} \text{A–H} & + & \text{M–OH} & \rightarrow & \text{A–M} & + & H_2O \\ \text{Acidic} & & \text{Metal} & & \text{Neutral metallic} & & \text{Water} \\ \text{substrate} & & \text{hydroxide} & & \text{detergent} & & \end{array} \qquad \text{(Reaction 7.1)}$$

A–M is the neutral salt of an acidic detergent substrate and may also be referred to as the soap or surfactant. The normally neutral soap can also be slightly acidic or basic, depending on the acid strength of the substrate and the base strength of the metallic hydroxide: metallic oxide can also be used. In general, the soap is the stoichiometric reaction product of one chemical equivalent of an acid substrate plus one equivalent of metal base.

Basic metal detergents are made in a manner similar to forming the neutral detergent. The metal hydroxides used in these basic detergents are typically divalent in character. For example, calcium, magnesium or barium, have been used; however, monovalent sodium versions can also be made. The basic detergent illustrated below contains 100% more base (on a chemical equivalent basis) than a neutral detergent, Reaction (7.2):

$$\begin{array}{ccccccc} \mathrm{A{-}H} & + & \mathrm{HO{-}M{-}OH} & \rightarrow & \mathrm{A{-}M{-}OH} & + & \mathrm{H_2O} \\ \begin{array}{c}\text{Acidic}\\ \text{substrate}\end{array} & & \begin{array}{c}\text{Divalent metal}\\ \text{hydroxide}\end{array} & & \begin{array}{c}\text{Basic metallic}\\ \text{detergent}\end{array} & & \text{Water} \end{array} \qquad \text{(Reaction 7.2)}$$

During the early 1950s, methods were discovered by which fully oil soluble detergents could be prepared that contain up to 30 times more metal than the normal neutral detergents. A number of terms, such as overbased, superbasic and hyperbasic, have been used to describe this class of detergents. In contrast to the simple basic detergents, there is no valence restriction on the metal for the formation of overbased detergents [4, 5]. Reaction (7.3) describes a typical method of preparing overbased detergents, where M is a monovalent metal:

$$\begin{array}{ccccccc} \mathrm{A{-}M} & + & 2x\,\mathrm{M{-}OH} & \xrightarrow[\mathrm{CO_2}]{\text{Promoter}} & \mathrm{A{-}M} \bullet x\,\mathrm{M_2CO_3} & + & x\,\mathrm{H_2O} \\ \begin{array}{c}\text{Neutral}\\ \text{metallic}\\ \text{detergent}\end{array} & & \begin{array}{c}\text{Metal}\\ \text{hydroxide}\end{array} & & \begin{array}{c}\text{Overbased}\\ \text{detergent}\end{array} & & \text{Water} \end{array} \qquad \text{(Reaction 7.3)}$$

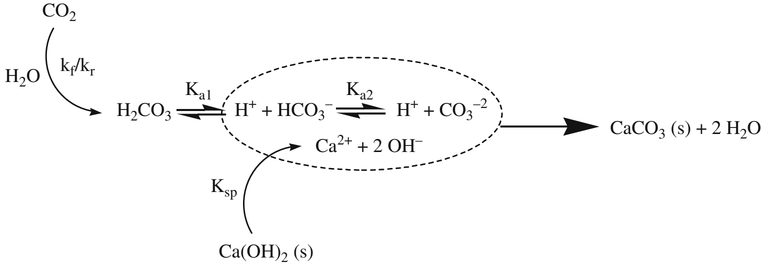
The number of chemical equivalents, x, of metal hydroxide, M–OH, can be varied from $x = 1$ to $x = {\sim}30$. The metal hydroxide can also be different than that used to prepare the neutral salt. Alternatively, a metal oxide, instead of a metal hydroxide, may be used as the starting raw material. In this case, the oxide is first hydrated to form the hydroxide in situ before the carbonation reaction takes place.

The manufacture of overbased detergents generally involves the reaction of certain promoters, catalysts or solvents with the acidic or neutral substrate and a large excess of metallic base in oil or organic solvent, followed by heating, solvent removal and filtration steps. Prior to filtration, reaction with an inorganic acid or acid anhydride, most commonly CO_2, is used to increase the amount of metal base colloidally dispersed in the filtered product. Although the process using carbon dioxide to produce a colloidally dispersed metal carbonate dominates commercial manufacture of overbased detergents, there are other anions besides carbonate that can be used in overbased detergents for lubricants. Among these are sulphite, derived from sulphur dioxide [6], and borate, derived from boric acid [7].

Many materials have been used as promoters or catalysts for the overbasing processes, including halides, alcohols, phenols, ketones, alkanolamines and carboxylic acids [8].

7.2.4 Overbasing Description

The detergent substrate is more than just a detergent. It is also needed to create reverse micelle reaction vessels during overbasing and to provide oil solubility/stability to the metal carbonate particles that are formed during overbasing. During this process, an enormous number, approximately 10^{20} per cm^3, of reverse micelles carry the promoters into the oil. These micelles are the key to overbasing. These polar reaction vessels allow the base to dissolve and dissociate into individual ions, from which the tiny overbased detergent nanoparticle is formed. When the metal hydroxide is added, it does not immediately dissolve into the micelle. Rather, it enters gradually, to replace the hydroxide that is consumed in the neutralization of H_2CO_3, Reaction scheme (7.4). The metal carbonate is insoluble, so once formed, it precipitates immediately. This precipitation is the driving force for bringing in more metal hydroxide and CO_2, making mass transfer an important processing variable [9]. Since all these reactions occur within the micelle, the size of the resulting metal carbonate particle is thus governed by two factors: (1) the size of the reverse micelle and (2) the number of micelles that collide to form metal carbonate aggregates [10]. Neutron scattering experiments show that the primary size of the



$K(CO_2) = k_f/k_r = 0.03\ s^{-1}/20\ s^{-1} = 0.0015$

$pK_{a1} = 6.35$

$pK_{a2} = 10.33$

$K_{sp}\ Ca(OH)_2 = 5.02 \times 10^{-6}$

$K_{sp}\ CaCO_3 = 3.36 \times 10^{-9}$

Reaction scheme 7.4 Pathway to form $CaCO_3$ from hydrated lime and CO_2 [13]

detergent particle is between 5 and 10 nm [11]. Molecular simulations show that overbased sulphonate detergents are spherical, Fig. 7.2, whereas overbased phenate detergents self-assemble into more rigid, disk-shaped structures [12].

The type of carbonate formed during the widely used carbon dioxide overbasing process is also important. In order to make an overbased calcium detergent that is soluble in mineral oil, it is important for most of the metal carbonate to exist in the amorphous form. It has generally been found that if crystalline calcium carbonates are incorporated in overbased detergents in any significant quantity, the mineral oil solubility characteristics are poor. However, a process to make a soluble crystalline calcium carbonate detergent was recently published [14]. In general, the solubility differences between amorphous and crystalline overbased magnesium carbonate detergents are less dramatic.

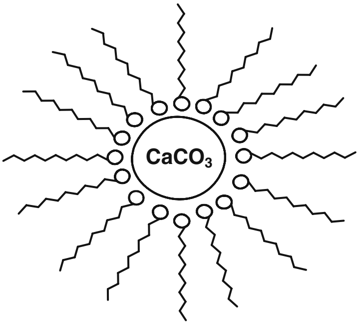


Fig. 7.2 Representation of a lubricant detergent reverse micelle, with the polar head of the detergent substrate oriented towards the centre of the micelle

Table 7.1 shows the infrared assignments for some of the common metal carbonates. Significant amounts of impurities can cause the infrared peaks to shift noticeably, so X-ray diffraction is still the most reliable analytical tool for crystal form assignment. Additional information on infrared absorption of carbonates [15], relative thermodynamic stabilities and transformation between phases has been published [16, 17].

Table 7.1 Characteristic infrared bands of group II metal carbonates

Metal	Carbonate form	Infrared assignments, wave numbers, cm^{-1}
Calcium	Amorphous	858 (broad)
Calcium	Vaterite	873
Calcium	Aragonite	Doublet 850/840 and 709
Calcium	Calcite	881 and 709
Magnesium	Amorphous	858
Magnesium	Crystalline*	Doublet: 848/840

*This crystalline form of magnesium carbonate is oil soluble when part of a detergent.

7.2.5 Detergent – Chemical Definition

Commonly, overbased substrates have been defined by the amount of total basicity contained in the product, for example, a 300 TBN (total base number) calcium sulphonate. Base number is defined in terms of equivalent amount of potassium hydroxide contained in the material. A 300 TBN calcium sulphonate contains base equivalent to 300 milligrams of potassium hydroxide per gram, or more simply, 300 mg KOH/g. This is the most convenient way to measure the amount of base present in oil, in a medium where pH is relatively meaningless and the primary base is not water soluble.

The use of TBN alone in defining an overbased detergent is quite misleading. To properly define an overbased detergent, three parameters of the basic material must be determined. Base number, per se, does not specify the metal ratio, that is, the ratio of metal base to substrate, the amount of neutral detergent or soap or the molecular weight of the substrate used.

Calcium overbased sulphonates are useful in illustrating this concept of overbased detergent definition. In addition to the molecular weight of the substrate, two of the following parameters must be specified to define the overbased sulphonate:

- percent sulphur
- total base number
- metal ratio
- percent calcium
- percent neutral detergent soap

The following series of general mathematical formulae are useful in understanding the parameters given above. Using overbased sulphonate substrate systems as the example, the general formula for a calcium overbased sulphonate is:

$$(\mathrm{RSO_3})_a\mathrm{Ca}_b(\mathrm{OH})_c(\mathrm{CO_3})_d$$

where a, b, c and d represent moles of the various functions.

Based on this formula, the following mathematical expressions can be used, Equations (7.1)–(7.3):

$$\text{Metal ratio} = \frac{2b}{a} \qquad \text{(Eqn. 7.1)}$$

$$\text{TBN (mg KOH/g)} = \frac{56{,}100 \times (2b - a)}{\text{sample weight}} \qquad \text{(Eqn. 7.2)}$$

$$\text{Percent soap} = \frac{\text{weight } [(\mathrm{RSO_3})_2\mathrm{Ca}]}{\text{weight [sample]}} \times 100 \qquad \text{(Eqn. 7.3)}$$

Although chemical descriptions of detergents are important for complete understanding, it is vital to recognize that practical performance features of the detergents govern the selection of the materials to use. Two detergents with the same TBN, molecular weight, metal ratio, etc. may have widely different performance characteristics. The simple chemical descriptions of detergents given above, while easy to quantify, do not provide a method of measuring performance. Other features of detergent chemical composition, including particle size, degree of crystallinity and the detailed chemical structure of the substrate, are needed to begin to understand detergent structure–performance relationships. The detailed chemical structures of detergents, especially overbased detergents, are difficult to elucidate completely. Recently, a variety of advanced techniques have been applied to this challenging problem, including X-ray photoelectron spectroscopy, XPS, time-of-flight secondary ion mass spectrometry, ToF-SIMS, energy-filtered transmission electron microscopy, EFTEM and X-ray absorption near-edge structure, XANES [18].

7.2.6 Substrates

The most commonly used detergents are derived from sulphonic acids. Two types are currently produced: natural sulphonates and synthetic sulphonates.

Natural sulphonates are not, by themselves, naturally occurring but were historically obtained as by-products of white oil manufacture. In recent years, however, they have been produced as first-intent products. Normally, natural sulphonates are obtained as the neutral sodium salts. These materials have also been referred to as petroleum sulphonates or mahogany acid soaps. Reaction sequence (7.5) shows the formation of natural sulphonates:

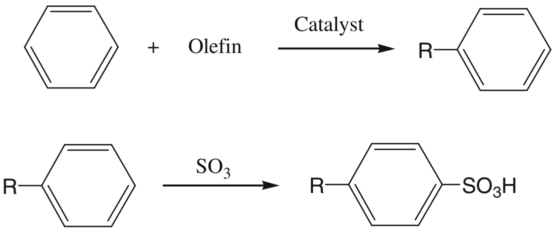
$$\text{Mineral oil} + \text{sulphuric acid} \rightarrow \text{white oil} + \text{sulphonic acid mixture}$$

$$\text{Sulphonic acid mixture} + \text{NaOH} \rightarrow \text{Mahogany acid soaps} + \text{green acid soaps}$$

(Reaction sequence 7.5)

Mahogany acid soaps are oil soluble, whereas green acid soaps, so named because of their characteristic colour, are water soluble. The use of natural sulphonates in lubricants has decreased in recent years, mainly due to cost and availability issues. Synthetic sulphonates have replaced them where possible, although a demand for natural sulphonates remains in certain applications.

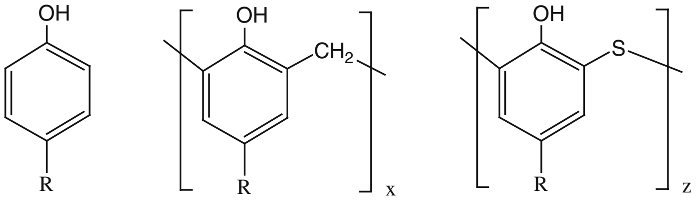
Synthetic sulphonates, in contrast, are derived from the sulphonation of feedstocks not derived directly from petroleum. The feedstocks commonly used to prepare this class of sulphonates have been polydodecyl benzene bottoms (by-products of household detergent manufacture) or alkylated benzenes produced specifically as feedstocks for lubricant additive sulphonates. The following generalized reaction sequence, Reaction sequence (7.6), describes the formation of a synthetic alkylate and sulphonation with sulphur trioxide [19], to yield the synthetic sulphonic acid:



(Reaction sequence 7.6)

where R is a linear or branched aliphatic hydrocarbon radical derived from ethylene, propylene or butenes and most commonly contains, on average, between 15 and 40 carbon atoms. To illustrate the topics described above, Table 7.2 summarizes the compositional ranges typically or historically observed in sulphonate lubricant additives.

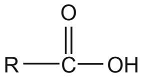
Phenates and phenate sulphides: Alkylphenols and substituted alkylphenols have been utilized for some time as substrates for the preparation of detergents. In addition to functioning as detergents, substituted phenates exhibit substantial antioxidant properties.



where R = aliphatic hydrocarbon radical containing between 5 and approximately 30 carbon atoms.

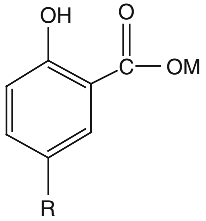
Alkylphenols are weak acids, but substitution on the alkylphenol with methylene or sulphur increases the acidity. The methylene-substituted phenates originate from a condensation product between the alkylphenol and formaldehyde. Phenate sulphides can be obtained by at least three sulphurization reagents: (1) sulphur monochloride, (2) sulphur dichloride and (3) elemental sulphur. The percentage of sulphur contained in a phenate sulphide detergent directly dictates the chemistry of the detergent because of the variable ratio of sulphur atoms to alkylphenol substrate and the variety of ways the sulphur atoms can be attached to the alkylphenol. Phenol detergents are more difficult materials to describe based on analytical data. Nevertheless, the same chemical concepts applied to sulphonates also apply to phenates. Table 7.2 summarizes the compositional ranges typically observed in phenate lubricant additives.

Carboxylates: High molecular weight carboxylic acids were the first substrates used to prepare detergent additives. Basic and overbased calcium alkylcarboxylates are still used in certain applications; a variety of other metal salts have also been used. The carboxylic acid can be described by the following general structure:



$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

Salicylates are a special class of carboxylates and can be described by the general structure below: the alkyl hydrocarbon radical R typically varies from 12 to 30 carbon atoms. Salicylates are a combination of phenate and carboxylate chemical functions. The chemical process generally used to prepare these substrates is known as the Kolbe–Schmitt reaction and involves the high-temperature reaction of an alkali metal phenate and carbon dioxide [20]:



As seen previously, a clear chemical definition of a carboxylate or salicylate is difficult to make based on a simple chemical analyses of the detergent. The same concepts that apply to sulphonate detergents also apply to these detergents. To illustrate how diverse the broad category of lubricant detergent can be, the typical ranges of parameters for commercially available detergents are collected together in Table 7.2.

Table 7.2 Range of typical detergent lubricant additives

	Range		
Parameter	Sulphonates	Phenates	Carboxylates
TBN, meq KOH/g	0–500	50–400	50–400
Soap content, %	10–50	30–50	10–45
Metal ratio	1–30	0.8–10.0	1–10
Common metal cation	Ca, Mg, Na	Ca	Ca, Mg
Percent sulphur	0.5–4.0	0–4	–
Sulphonic acid molecular weight	375–700		
Alkyl phenol molecular weight*		160–1,000	
Carboxylic acid molecular weight			250–1,000

*This molecular weight does not include phenol units connected together by, for example, sulphur- or formaldehyde-derived units; it is simply the molecular weight of the monoalkylphenol.

Although a wide variety of overbased detergents is possible, performance of a particular detergent depends on a number of factors that vary with the application, including:

- type of detergent soap (sulphonate, phenate, carboxylate),
- molecular configuration of the hydrocarbon portion of the detergent,
- molecular weight of the detergent soap,
- metal ratio of the detergent and
- the metal used.

7.2.7 Performance in Lubricants

For crankcase engine oils, which include passenger car, heavy-duty diesel, marine diesel and stationary gas applications, detergents provide several key performance functions. One of the key primary functions of overbased detergents is to neutralize acidic combustion by-products. In all reciprocating piston internal combustion engines, gases from the combustion chamber are forced through the piston ring pack and into the crankcase where they interact with the lubricant. These combustion gases and by-products contain components such as oxides of sulphur, derived from the sulphur content of fuels. Particularly in diesel engines, these sulphur oxide compounds interact with oxidized components from fuel and base oil to produce sulphuric acid and organic acids.

Another form of combustion by-products comes from oxides of nitrogen, derived from the high-temperature combination of nitrogen and oxygen from the intake air. These by-products are predominant in gasoline engines in which the oxides of nitrogen materials can further react with water, from the combustion process, oxidized oil and fuel, and soot, if it is present, to produce engine sludge and piston varnish. Obviously, these acidic combustion gases and by-products are detrimental to the extended life of both engine components and the lubricant itself. They can increase rusting of steel parts and corrosion of bearings. Consequently, the use of high TBN, overbased detergents can combat these problems. The mechanism of acid neutralization has been investigated using FTIR [21], FTIR and stopped flow UV/VIS spectroscopy [22] or by direct observation using a capillary video-microscopy system [23]. Care must be taken when formulating to use an appropriate mix of detergents for acid control and corrosion performance. The use of several appropriate detergents in a lubricant for excellent engine rust control and bearing corrosion performance may not necessarily be favourable for attaining, for example, good fuel economy performance, as measured in the ASTM Sequence VIB engine test.

A second function of a detergent is to retard deposit formation on engine parts, especially parts that are operating at high temperature, such as pistons and piston rings. The selection of detergents to provide the best piston and ring cleanliness is highly dependent on the temperature of the piston-ring area, the metallurgy of the piston, the ring pack design and the base stock of the lubricant being tested. Metallurgy variances in engine designs, such as aluminium versus articulated steel diesel pistons, complicate proper detergent selection. A particular mixture of detergents may be excellent performers with aluminium hardware but may perform only marginally with steel hardware [24].

Some types of detergents perform additional functions in an engine oil formulation. For example, sulphur-coupled alkylphenols enhance high-temperature oxidation inhibition. Due to their specific structure and thermal stability, these detergents help prevent oxidation of the lubricant under high-speed and engine load conditions, resulting in a lower viscosity increase of the oil. High-temperature oxidation inhibition also helps with the detergent's ability to enhance cleanliness.

In crankcase applications, the best overall cost and performance compromise using a selected combination of detergents in a lubricant depends on many factors. Several of these factors entail complete engine performance, customer desires and regulations, including the maximum total amount of metal and sulphur allowed in a lubricant as set by specification requirements [25].

In driveline lubricant applications, the detergent has important functions even though there are no combustion gases in this environment. Driveline lubricants usually must operate properly for the life of the vehicle whilst in contact with friction elements composed of cellulose, carbon, sintered metal and other materials. Commonly, these friction elements are shifting clutches and bands, controlled-slip torque converter clutches, power take-off clutches and manual transmission synchronizer elements. In order to function properly, these materials must retain their original surface morphology as much as possible. Overbased detergents help to retard corrosion of the metallic friction elements [26] and accumulation of lubricant degradation products and other contaminants in the porous surface structures of these materials.

The detergent in a transmission or farm tractor hydraulic fluid formulation is a key component for setting the frictional properties of the fluid, including the dynamic coefficient of friction, the static coefficient of friction and the slope of a friction versus sliding speed curve with a particular set of friction elements. Even more importantly, a detergent retains these properties for extended periods of time [27–29].

Elastomeric sealing elements are also used extensively in all types of transmissions and hydraulic equipment. Often these elastomers are particularly sensitive to the build-up of acidic oxidation and degradation products in the lubricating oil. The presence of an overbased detergent in the lubricating oil often greatly extends the life of the seals due to the suppression of acid build-up [30, 31]. Engineering plastics are also used in transmissions for thrust washers, filter screens and gears that operate speedometer cables or mechanical governors. Nylon gears tend to be sensitive to acid build-up in the lubricant at elevated temperatures [32]. Overbased detergents have a similar protective effect on these components and extend their useful working lives.

7.2.8 Summary

Lubricating oil detergents are metal salts of organic surfactants that provide corrosion protection, deposit prevention and numerous other performance enhancements to lubricant formulations. In overbased detergents, these organic metal salts further incorporate a colloidally dispersed, basic inorganic component, which imparts basicity to formulations to neutralize acidic contaminants. The degree of overbasing and the size and form of the inorganic component impact the performance features of the detergents. A wide variety of organic molecules and inorganic components can be used in lubricant detergents, but sulphonate, phenate and salicylate types incorporating calcium carbonate are the most widely used. The appropriate choice of detergent type and level in a lubricant is highly dependent on the specific application, and combinations of several types are generally needed to optimize both performance and cost.

7.3 Dispersants

7.3.1 Introduction to Dispersants

Like detergents, dispersants have been used for many years in fuels and lubricant applications. Both are based on a traditional surfactant structure, but the chemistry of each is markedly different. This chapter has already discussed detergents in detail, highlighting the various metal-containing counterions and substrates employed. The aim of this section is to provide a similar review of dispersants, including mode of action, synthesis and additional effects these additives have on an oil formulation.

The first dispersant additives were introduced during the 1950s to help keep engines clean in response to short distance/stop-and-go driving conditions and larger horsepower engines, leading to excessive viscosity increases in passenger car motor oils. By adding dispersants to the formulation, the polar debris generated by both fuel and oil oxidation was maintained in solution, suppressing the thickening otherwise observed. Dispersants are now commonly found in a range of other automotive fluids, including fuels, automatic transmission fluids and gear oils. Specific uses will be explained in more detail later in this chapter, with initial emphasis given to engine oil applications since they are the largest commercial users. However, many of the principles defined here will also be applicable to these other applications.

7.3.2 Dispersant Mode of Action

As the name implies, a dispersant is designed to keep potentially harmful debris dispersed within the lubricant during engine operation. This mediates the otherwise negative effects such as viscosity thickening, wear and filter plugging which these contaminants would have on the oil. The deposit-forming debris can then be removed periodically by an oil change. In an engine environment, the dispersant can be considered to handle two main deposits: soot and sludge. Fortunately, most of the dispersant types described in this chapter are adept at handling both:

- *Soot* is typically formed in the combustion chamber of diesel engines due to incomplete oxidation of the fuel during ignition. Soot then builds up in the crankcase, leading to problems of oil thickening. These particles also tend to be granular and abrasive in nature and cause wear to the metal surfaces of engine components.

- *Sludge* is typically formed in the lubricant of gasoline passenger car engine oils and is generally finer in nature than soot. It results from the thermal oxidation of oil and the blowby gases from the combustion chamber containing partially burned fuel. These by-products can then flocculate in hotter parts of the engine or in the colder regions by the co-action of water.

Both soot and sludge lead to a detrimental increase in the oil's viscosity. Additionally, varnishes and lacquers form if these oxidized products condense on hot surfaces of the engine. Thus, dispersants have been designed to contain a polar head group attached to a long hydrocarbon tail that gives oil solubility. Their mode of action is then dictated by an interaction between the surfactant and the surface of the polar contaminants, as in Fig. 7.3. Nominally, oxygen, or more typically nitrogen, is used in the head group.

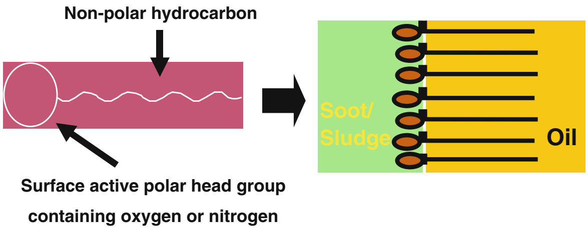


Fig. 7.3 Schematic representation of a dispersant and mode of action

Dispersants hinder agglomeration via two mechanisms: steric and electrostatic stabilization. In the first case, once the polar head group has been adsorbed onto the surface of the dirt particle, the tail provides a physical barrier to attraction. This separates the small particles and prevents them from contacting with others and increasing in size, as in Fig. 7.4.

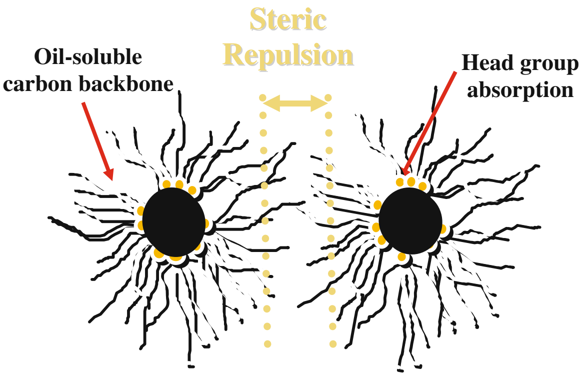


Fig. 7.4 Steric stabilization of engine oil contaminants

Dispersants can also induce a charge on the dirt particles, and this is how the electrostatic stabilization effect is believed to work. So contaminants such as sludge that have acidic groups and dispersants that contain basic amine sites interact, forming salts. Agglomeration is then inhibited by electrostatic repulsion of the negatively charged dirt particles, as in Fig. 7.5.

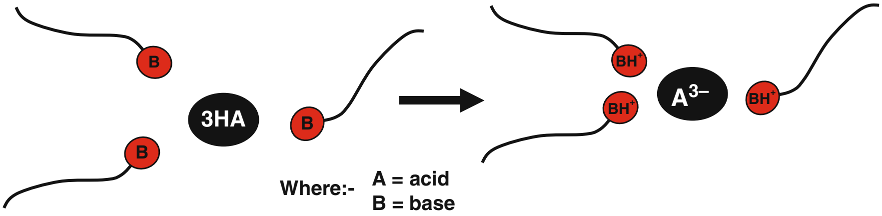


Fig. 7.5 Electrostatic stabilization of engine oil contaminants

These mechanisms show why dispersants have one of the highest additive treat rates in an engine lubricant package; activity is related to concentration. Typical treat rates range from 4 to 8% in fully formulated engine lubricants, reflecting the need to maintain the lubricant dispersion ability over long oil drain periods. Figure 7.6 further highlights the effect of treat rates on performance. The Sequence VE is an industry standard test used to evaluate an engine oil's ability to handle sludge, among other things [33]. Three different end of test drain oils are shown for particle growth after the 288-h run time. These formulations contained 1.0, 2.3 or 5.0% of dispersant and show the positive effects of higher treat rates on inhibition of particle growth.

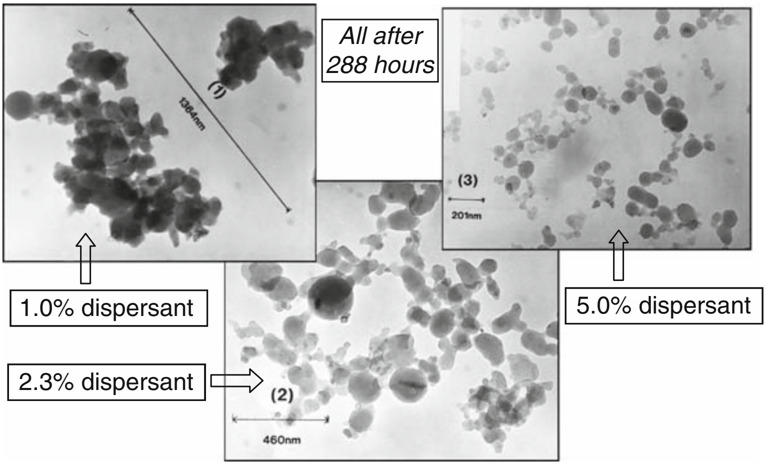


Fig. 7.6 Sludge particle growth in a sequence VE test

7.3.3 Synthesis of Dispersants

Figure 7.7 is a modified surfactant model showing how the two core elements of a dispersant are put together. Unlike the previous diagram, a bridging hook group has now been included that connects the hydrocarbon tail with the polar head group. Today, the majority of manufactured dispersants require this additional functional group.

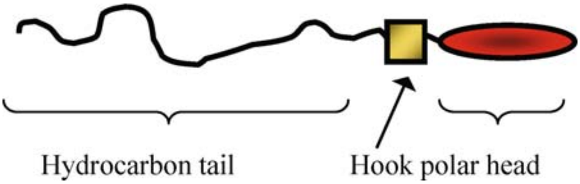


Fig. 7.7 Modified surfactant dispersant structure

For most dispersants, the hook is either maleic anhydride (MAA) or phenol, and these are first attached directly to the hydrocarbon tail. For the latter, this is then reacted with formaldehyde and polyamines to form substituted hydroxylbenzyl polyamines, known as Mannich products. Alternatively, the MAA groups can be reacted either with alcohols to form esters or with amines to form imides/amides. In general, the hydrocarbon tail of choice is polyisobutylene (PiB) for reasons including cost effectiveness and clean decomposition at high temperatures. Molecular weights used range from 500 to 10,000 amu but are most commonly 1,000–2,500 amu. These maleic anhydride intermediates are known as polyisobutylene succinic anhydrides or PiBSAs. The dispersant products are known as either succinimides or succinic esters. Further details for each dispersant type will be provided below. More recently, dispersant viscosity modifiers or DVMs have also been used in engine lubricant formulations [34, 35]. These typically contain an alternative polymer backbone, such as ethylene–propylene, and have various polar-containing substrates grafted along the side chain. The molecular weights are also much larger, typically 10,000–40,000 amu. So, although these additives deliver dispersant properties to a formulation, they are sufficiently chemically different to not be considered further in this chapter.

Polyisobutylene succinic anhydride (*PiBSA*) *formation:* PiBSAs are the key intermediates in forming succinimides and succinate esters. Dependent on how the polyisobutylene is made, one of two routes is used for the reaction with maleic anhydride. PiBs produced using boron trifluoride, BF_3, as a catalyst give products favouring formation of vinylidene end groups. The use of aluminium trichloride, $AlCl_3$, provides mostly the tri/tetra substituted end groups, the typical end groups formed with either catalyst are shown in Fig. 7.8 [36]:

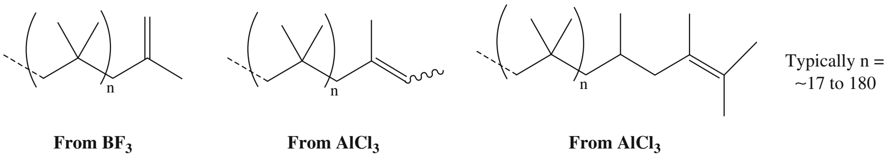
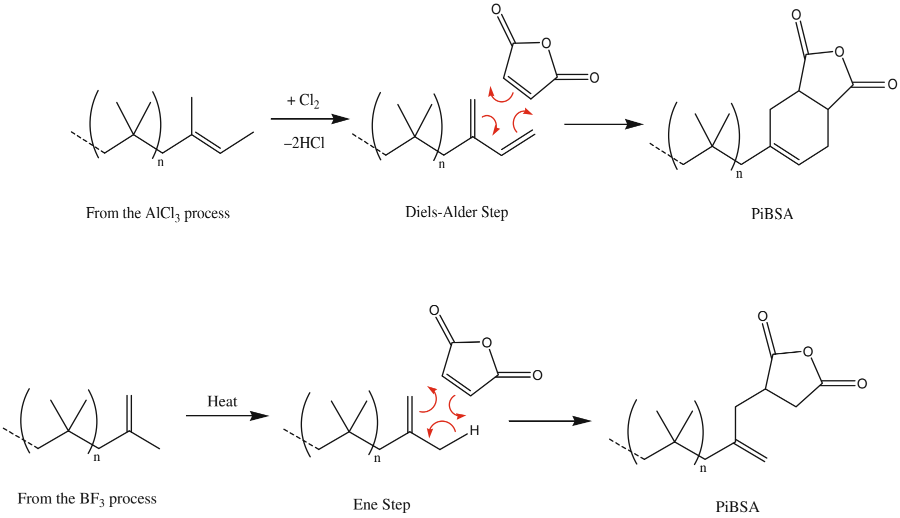


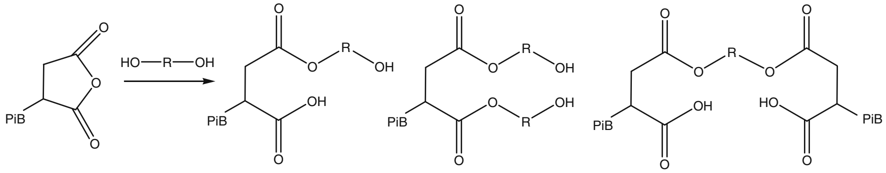
Fig. 7.8 Various end groups of polyisobutylene

Dependent upon the PiB source, conversion to the PiBSA is promoted by either a Diels–Alder or an ene process. Using $AlCl_3$-based PiB, an equivalent of chlorine and maleic anhydride per double bond is added. Elimination of two equivalents of hydrogen chloride form a diene due to the double bond substitution of the major olefin end groups. This sets up a facile Diels–Alder reaction with the maleic anhydride to form the PiBSA. Alternatively, using the BF_3-sourced PiB, which contains high levels of vinylidene end groups, excess maleic anhydride is added and the two materials are heated together at high temperature. This forces a reaction with the less-substituted vinylidene double bond giving the PiBSA product. As can be seen from Reaction sequence (7.7), these two routes give subtle differences to the head group architecture [37, 38]. This is extremely useful because both types of molecules can provide different performance advantages depending on the application.



Reaction sequence 7.7 Diels–Alder and -ene routes to PiBSAs

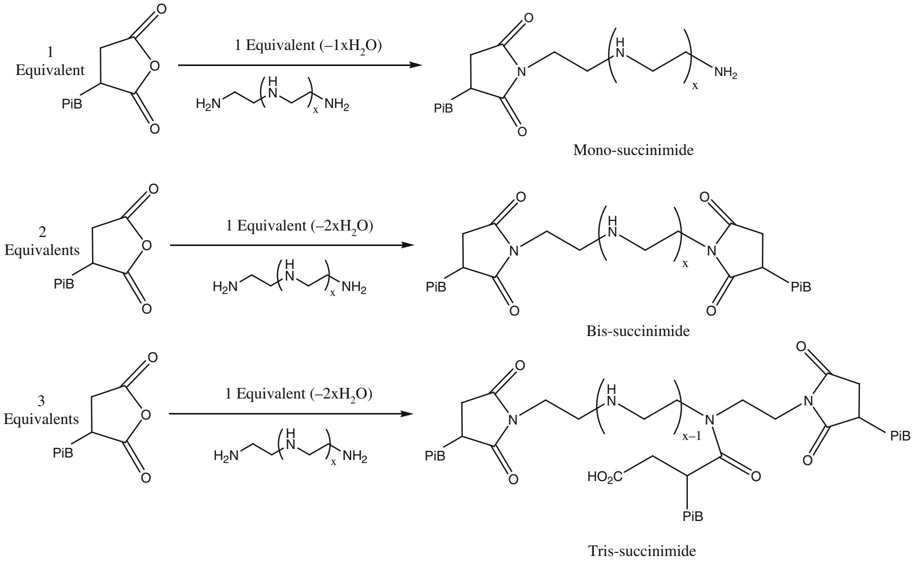
Polyisobutylene succinic esters – Succinic esters are formed by the reaction of PiBSAs with alcohols [39]. In general, polyols are used which can form different products dependent upon alcohol equivalents and processing conditions. These include the monoester, diester and coupled product, Reaction (7.8), where the PiBSA head group has been modified to a generic structure for simplicity.



Reaction 7.8 Succinic ester dispersants

Polyisobutylene succinimides: Succinimides are by far the most common dispersants used in engine oil formulations today. Formation involves the reaction of a PiBSA with a polyamine. In general, these are ethyleneamines made by an ethylene dichloride/ammonia process [40]. This generates a mixture of oligomeric species, which are purified by fractional distillation. Lower molecular weight fractions such as diethylenetriamine (DETA), triethylenetetraamine (TETA) and tetraethylene pentamine (TEPA) are separated to form cuts of higher purity. The mixture remaining after distillation is referred to as the bottoms or heavies. All fractions, including the bottoms, can be used in dispersant synthesis. Ethyleneamines can also be made by reductive amination. Today, this process struggles to generate the heavier amines that are important for dispersant synthesis.

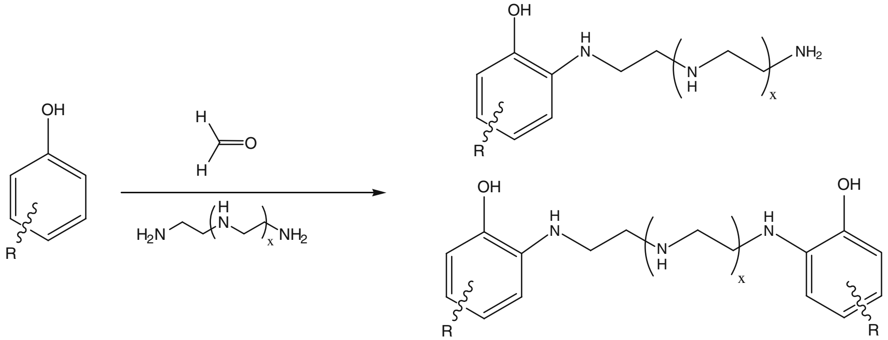
In addition to polyamine variation, another key parameter to succinimide formation is the level of nitrogen in the final product, i.e., the amount of amine reacted with PiBSA can vary. Reaction sequence (7.9) shows the three syntheses and common structures used to represent dispersants using the typical ratios of these reactants. A generic polyamine is shown, and the ratio to PiBSA varies from 1:1, 2:1 to 3:1, generating the key mono-, bis- and tris-succinimides, respectively. In each case, the primary amine reacts preferentially with the PiBSA unit, eliminating water and forming the imide. For the tris model, after all the primary nitrogens are consumed, a secondary amine opens up the additional anhydride group to form an amide. In reality, this situation is more complex, with branched and cyclic species also present in various amounts, dependent on the polyamine used. This means other side reactions will occur. However, these simplified models are still very important in interpreting dispersant performance in a particular application. These materials are typically processed directly in oil.



Reaction sequence 7.9 Synthesis and structures of succinimide dispersants

Succinimides can also be post-treated to provide additional performance properties; one of the most commonly used reagents is boric acid which delivers antiwear properties to a formulation [41]. Post-treatments with other maleic anhydride-containing co-polymers, such as polyoctadecene succinic anhydride, yield dispersants with enhanced viscosity credit [42]. Uses of other reagents, such as carbonates, lactones, sulphur dioxide, epoxides, oxalic acid and carbon disulphide, have also been disclosed [43].

Mannich-type dispersants: Named after the chemist who discovered this type of reaction, Mannich dispersants are the final ashless dispersants considered in this chapter [44]. Synthesis involves treating an alkylphenol with formaldehyde and a polyamine [45]. The alkylphenols are derived from reacting polyisobutylene or polypropylene with phenol under Friedel–Crafts conditions [46]. Molecular weights of the alkyl chain range from ~200 to 1,500 amu, with 1,000 amu being typical. Under the Mannich reaction conditions, an iminium ion is formed between the primary nitrogen of the polyamine and formaldehyde. Secondary amines also react, but the primary generally takes precedence. This species then undergoes alkylation with the phenol derivative, forming a carbon–carbon bond. Rearrangement of the keto–enol form regenerates the aromatic ring, giving the Mannich dispersant. Depending on reaction conditions, polyamine used and ratio of this amine to formaldehyde, various side reactions can also occur, Reaction (7.10). The most common of these is the dimer, which is also highlighted below. As with succinimides, post-treatment of these dispersants with a variety of reagents, such as boric acid, is possible [47].



Reaction 7.10 Synthesis of Mannich dispersants

7.3.4 Effects of Dispersants in Engine Oil Formulations

In addition to cleanliness, dispersants affect seal compatibility and copper/lead corrosion in engine oil formulations.

Seal compatibility: Elastomeric seals are essential parts of engine design for a number of reasons, including preventing leakage of oil from the sump. Due to good thermal stability and resistance to oxidation, fluoro-elastomers are commonly used for this application. They are formed by the polymerization of mixtures of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene. However, these materials are sensitive to dehydrofluorination across the polymer backbone, especially when in contact with basic amines [48]. The resulting unsaturation that forms is susceptible to oxidation and cross linking, leading to a loss of physical properties which is highly undesirable. Since the lubricant is in contact with the seal, basic amine sites from the dispersants are a major cause of this unwanted degradation. Dispersant type, nitrogen content and treat rate all influence the rate of this process. So, high nitrogen-containing dispersants used at high treat rates will generally be more aggressive to the seals. This is contrary to engine cleanliness requirements, which normally prefer higher treat rates and nitrogen levels. As a means to evaluate seal performance, a number of bench tests have been developed to mimic compatibility of the fluoro-elastomer with the lubricant. Tests for other seal material types are also available, but the dispersant effect is less pronounced [49]. This means that when formulating an engine oil, the dispersant factors mentioned above must be carefully balanced to allow optimal engine cleanliness while providing acceptable seal compatibility.

Copper/lead corrosion: Strictly speaking, polyamine dispersants have a corrosive effect on copper in an engine environment. However, zinc dialkyl dithiophosphates (ZDDPs) are always used in formulations of this type as antiwear agents. These react with the metal surface, forming protective polyphosphate layers in the engine. This passivates lead corrosion, but the breakdown products formed promote attack of copper. Matters are further complicated by complexation of the zinc with basic amine groups of the dispersant [50]. Using highly basic dispersants gives more ZDDP interaction, leading to less copper but more lead corrosion. This also positively affects seals since the basic nitrogen groups are tied to the metal. Alternatively, less basic dispersants provide less ZDDP interaction, leading to less lead but more copper corrosion. This means that although cleanliness is important, other properties of oil must also be considered. Therefore, as with seal compatibility, formulating dispersants into engine oils requires a careful balance of additive interactions to meet the optimal all-around performance required.

7.3.5 Dispersant Use in Other Fuel and Lubricant Applications

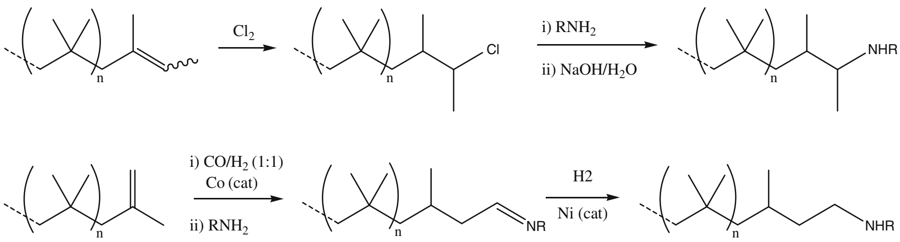
Together with engine oils, the other major industrial uses of dispersants are in automatic transmission fluids, gear oils and fuels. In general, the concepts developed in this chapter are also applicable to these applications.

Automatic transmission fluids, ATFs: Frictional behaviour is a key performance characteristic of an ATF. During operational lifetime, thermal and oxidation by-products can form in the lubricant. These have the potential to fill the porous holes found in the surface of the transmission, causing the clutch plates to slip. A dispersant is necessary to keep these by-products suspended in the oil, and typical treat rates vary between 1 and 6%. Additionally, the dispersant can positively affect friction if chosen correctly. A number of reasons for this have been proposed, including the polar head group interacting with the material surface, thereby acting as a friction modifier; the dispersant controlling what goes onto this surface from the additive pack; or a dispersant–additive interaction generating a more active product. Seal testing is also used for these fluids, although seals tend not to be such a big issue as in engine oils. This allows the use of higher nitrogen-containing dispersants in the formulation, which helps additive package compatibility.

Gear oils: Many of the characteristics described for ATFs are also applicable to gear oils. The primary application is to suspend dirt and prevent deposits caused by breakdown of the lubricant. Secondary applications are the frictional properties and additive package compatibility. Seals are also important, and in general, the dispersant is beneficial as it keeps the sealing grooves of these elastomers clean. However, as in engine oils, care has to be taken that the basic sites of the polyamine do not cause dehydrofluorination leading to seal degradation. Typical treat rates are between 0.5 and 3%, and again, higher nitrogen-containing dispersants are used than in engine oil applications. This high amine content, combined with the metallurgy of the gears, also positively impacts corrosion.

Fuels: Additives are used in both diesel and gasoline fuel applications to maintain operational cleanliness. Although dispersants chemically, they are generally referred to as fuel detergents. The primary reason for this is the surface cleaning mechanism that operates in these applications, i.e. the dispersant also acts like a detergent. In diesel engines, an injector sprays a fine mist of fuel either directly or indirectly into the combustion chamber. By-products of incomplete combustion, such as soot or thermal/oxidative degradation products within the fuel injection system, can build up on metal surfaces of the injector leading to nozzle fouling. This disrupts the metered fuel volume or the uniformity of the spray pattern, leading to poorer combustion and lower engine efficiency. In gasoline engines, fuel is sprayed from the injectors onto inlet valves in port fuel-injected, PFI, engines or directly into the combustion chamber in direct-injection, spark-ignited, DISI, engines. In both cases, oxidative degradation of the fuel can foul injectors and spray patterns are disrupted, resulting in poor fuel vaporization, disruption of the desired air–fuel ratio and a similar loss of engine efficiency. In PFI systems, fuel-derived deposits also dominate the build-up on inlet valves (oil-derived deposits dominate inlet valve deposits in DISI systems), resulting in similar problems.

Deposits in both diesel and gasoline applications are controlled by adding small quantities of the detergent directly to the fuel. Typically, treat rates are at the parts per million level, and two modes of action take place. In keep-clean mode, the surfactant nature of the dispersant adsorbs onto the metal surface and prevents carbonaceous deposit formation. In the second mode of action, clean up, the dispersant molecules form micelles around the deposits, facilitating their removal. In terms of dispersant type, diesel applications tend to use mono-succinimides with high base numbers since seal performance is less important [51]. Gasoline detergents are more varied in chemistry and can be the PiB phenol or Mannich chemistries described for engine oils above [52, 53]. Another class of detergents for fuels not yet covered are also used. These are known as PiB amines and are formed by the two routes shown in Reaction (7.11). Again, the method is dependent on the source of polymer used. With $AlCl_3$-derived PiB, chlorination, followed by displacement with an amine, gives the product [54]. Alternatively, using BF_3-derived PiB with higher vinylidene content, the product is obtained by carbonylation, followed by reaction with an amine and reduction with hydrogen [55].



Reaction 7.11 Synthesis and structures of PiB amine fuel detergents

In addition, gasoline detergents are normally employed with carrier fluids or fluidizers and are rarely used without them. These help reduce inlet valve sticking and may also help to clean the detergent/soot mix from the surface [56].

7.3.6 Summary

The primary function of a dispersant is the stabilization of contaminants generated during a lubricant's lifetime. This ameliorates the negative effects these particles would have on the oil's properties, such as viscosity increase, wear and filter plugging. Like traditional surfactants, a dispersant will contain a polar head group connected to a non-polar side chain, with a range of molecule types available. This reflects the need to formulate for many applications with different performance needs. However, with tougher future lubricant specifications and the introduction of new engine hardware, the development of innovative dispersant technologies will undoubtedly be required.

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Part III
Applications

Chapter 8
Industrial Lubricants

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Abstract 'Industrial lubricant' gaseous, liquid and solid products cover many applications. A new systems analysis approach is used combining heterogeneous catalysis and tribochemistry. Bearing lubricant applications are discussed in terms of the bearing film thickness and tribological regimes, for liquid and solid lubricants. Compressor and vacuum pump lubricant applications are described. The various classes of hydraulic fluids for industrial applications are explained. The properties, applications and selection of various industrial lubricants for different gears are described. Steam and industrial gas turbine lubricant formulations are discussed and the effects of their degradation products, particularly for valves and filters, are presented. Metalworking lubricant applications are divided into cutting and forming operations and their actions are described. Speciality applications such as process, textile, food-grade, slideway, cylinder and wire rope lubricants are explained.

8.1 Introduction

8.1.1 General Aspects of Industrial Lubricants

Industrial lubricants comprise a wide variety of products which, depending on their application, differ widely in their chemical and physical properties. It can be said that industrial lubricants involve all classes of lubricants applied in practice, including gases (mostly air and carbon dioxide, a future very special gas lubricant seems to be nitrogen), various liquid products (mineral oils, animal and vegetable oils, derivatives of tall oil fatty acids, synthetic oils, water-based fluids, etc.), greases (simple soap greases, complex soap greases, greases with pigments, minerals, polymers and other materials) and solid lubricants. The latter comprise inorganic compounds, (such as molybdenum disulphide, boron nitride, tungsten disulphide and many other chemicals and materials), solid organic compounds and materials (such as phthalocyanine and polytetrafluoroethylene), chemical conversion coatings and soft metals.

Furthermore, industrial lubricants make use of many additives which include practically all known additive classes used in other types of lubricants. In addition there are numerous additives developed specifically for industrial lubricants, particularly for water-based fluids such as glycerol esters and other eco-friendly

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ester types which are of particular present interest. A summary of developments in several areas of industrial lubricants involving either direct or indirect environmental considerations includes minimization of pollution and energy conservation [1]. Potential applications were examined for the tribopolymerization concept in developing eco-friendly anti-wear additives and lubricants, for example, 'green' lubricants for a variety of industrial applications. The tribopolymerization process has been described in detail as a boundary lubrication mechanism. It is difficult to overestimate the importance of eco-additives in formulating industrial lubricants and the final products of industrial eco-lubricants [2]. Most recent work has studied the anti-wear properties of *n*-butyl acrylate in hexadecane for steel–steel friction elements [3]. Clear evidence was found that tribopolymerization is initiated by low-energy electrons and the chain propagation was controlled by the alkyl radical. The precipitated tribopolymer was analysed using GPC, FTIR, NMR and TG to show that the tribopolymer with an extremely high molecular weight had a similar structure to products from regular polymerization. The amount of tribopolymer produced increased with the increasing sliding velocity of a pin-on-disc device.

High speed and lightly loaded plain bearings need a low-viscosity plain mineral oil, where the oil viscosity is essential to ensuring hydrodynamic lubrication. Higher loadings and lower speeds require higher viscosity oils. It is worth noting that base oil viscosity influences the wear prevention characteristics of some eco-friendly additives under extreme-pressure conditions and they are more effective in a less viscous oil [4]. From the lubricant chemistry view point, these oils are the simplest, composed of components derived from crude oil, mostly isoparaffinic, naphthenic, naphthenic aromatic and, to some extent, aromatic hydrocarbons, with all ring structures substituted by alkyl chains. Hydrocarbon viscosities depend on their molecular weights; for more details on mineral oils, see Chapter 1.

Apart from the simple lubrication of plain bearings, lubrication of tribological elements in moving contact under mixed and/or boundary friction requires very complex mixtures of appropriate mineral base oils and a number of possible additives. Selection of additives in formulating industrial lubricants involves consideration of the lubrication requirements of the equipment or the metal/process type of a metalworking operation. Although many products have been used as industrial lubricants, including lubricants developed for other applications, industrial equipment manufacturers recommend particular lubricants for specific applications. Thus, in recent years lactam compounds were found to be very effective anti-wear additives towards ceramic materials as well as metals; a new anti-wear additive group of lactams has been described with particular emphasis on caprolactam, the monomer of nylon 6 [5].

Industrial lubricants have a very diverse range of applications and overall they comprise the largest volume usage of lubricants. It is not possible to discuss all specific details associated with industrial lubricants in this chapter. As industrial lubricants based on mineral and synthetic basestocks are somewhat similar to motor oils, see Chapter 9, and are described elsewhere [6, 7], they will be discussed in general terms. Metalworking lubricants have also been described in a number of books [6–14]. The following current trends are predominant:

(i) the increasing use of Group II and III mineral oils in industrial lubricants to gain longer lubricant life,
(ii) increasing use of environmentally accepted and biodegradable lubricant base oils such as vegetable oils, synthetic esters and polyglycols together with other eco-friendly esters and additives such as sulphurized fatty materials of animal or vegetable origin and succinic acid derivatives,
(iii) increasing lubricant compatibility with contaminants such as water and trace amounts of zinc or calcium-containing additives,
(iv) protection of equipment against all wear under boundary conditions,
(v) limitation of zinc in effluent discharges from metal products and machinery facilities as it is a primary (toxic) pollutant.

8.1.2 Classification of Industrial Lubricants

Industrial lubricants include a very large number of specialized products from all lubricant classes. Therefore, with the exception of some lubricant groups, such as hydraulic fluids, it is rather difficult to classify them as clearly as, say, engine oils.

The majority of industrial oils for which viscosity is a significant criterion, for example fluid bearing lubricants, are classified according to the ISO 3448 viscosity grade classification, Table 8.1. This consists of 18 viscosity grades in the range 1.98–1650 mm^2/s, each grade represented by a whole number, obtained by rounding off the mid-point viscosity at 40°C, expressed in mm^2/s. No quality evaluation is implied by this classification.

Table 8.1 Viscosity grades for industrial lubricants, ISO Standard 3448

	Kinematic viscosity at 40°C, mm^2/s		
	Minimum viscosity	Maximum viscosity	Mid-point viscosity
2	1.98	2.42	2.20
3	2.88	3.52	3.20
5	4.14	5.06	4.60
7	6.12	7.48	6.80
10	9.00	11.00	10.00
15	13.50	16.50	15.00
22	19.80	24.20	22.00
32	28.80	35.20	32.00
46	41.40	50.60	46.00
68	61.20	74.80	68.00
100	90.00	110.00	100.00
150	135.00	165.00	150.00
220	198.00	242.00	220.00
320	288.00	352.00	320.00
460	414.00	506.00	460.00
680	612.00	748.00	680.00
1000	900.00	1100.00	1000.00
1500	1350.00	1650.00	1500.00

What are called ‘general machinery oils’ classified according to ISO viscosity grades encompass mineral oil products from light oils for spindle lubrication to heavy black oils for wire rope lubrication. ‘General machinery oil’ products cover the full range of speeds and loads used in industrial machinery, usually containing mineral oil raffinates of suitable thermochemical stability to provide long-term machinery lubrication, especially bearings. These oils are sometimes included in a group of machine lubricating oils together with slideway oils, multipurpose oils and lubricating oils for precision instruments and watches [8].

Another category consists of metalworking lubricants which, in many cases, are treated separately in conjunction with their tribology [9, 10]. These are not classified under the viscosity grade system since properties other than viscosity such as cooling and lubricating properties are much more important. A viscosity grade is not required as part of the identifying mark.

A further classification approach might include the categories of production engineering lubricants, such as machine tool and metalworking lubricants, lubricants for engineering components such as refrigerator, heat transfer and transformer oils and plant maintenance lubricants such as compressor, hydraulic, turbine and gear lubricants. ISO 6743-99 established a general system of classification for lubricants, industrial oils and related products, designated by the prefix letter ‘L’. Within class L, 18 families of products are defined, Table 8.2, according to each application area, to cover all the applications for which these products are used, as far as is possible.

Table 8.2 ISO 6743-99 classification of lubricants, industrial oils and related products

Part of ISO 6743-99	Family code	Family title
ISO 6743-0:1981	–	General
ISO 6743-1:2002	A	Total loss systems
ISO 6743-2:1981	F	Spindle bearings, bearings and associated clutches
ISO 6743-3:2003	D	Compressors
ISO 6743-4:1999	H	Hydraulic systems
ISO 6743-5:2006	T	Turbines
ISO 6743-6:1990	C	Gears
ISO 6743-7:1986	M	Metalworking
ISO 6743-8:1987	R	Temporary protection against corrosion
ISO 6743-9:2003	X	Greases
ISO 6743-10:1989	Y	Miscellaneous
ISO 6743-11:1990	P	Pneumatic tools
ISO 6743-12:1989	Q	Heat transfer fluids
ISO 6743-13:2002	G	Slideways
ISO 6743-14:1994	U	Heat treatment
ISO 6743-15:2007	E	Internal combustion engine oils
?	B	Mould release
?	Z	Cylinders of steam machines
IEC 61039	N	Insulating oils
ISO 6743-99:2002	–	General

To simplify industrial lubricant classification, the names of lubricants such as bearing lubricants, compressor lubricants, hydraulic lubricants, gear lubricants, metalworking lubricants, etc., derive from their application. These classifications are consistent with other lubricant categories, i.e. lubricants for internal combustion engines, aviation lubricants and marine lubricants.

8.1.3 A New Systems Analysis Approach to Modelling Industrial Lubricants

In boundary lubrication, solid surfaces are so close together that appreciable contact between opposing asperities is possible. Under these conditions, friction and wear are determined predominantly by interactions between the solid and the liquid phases [15]. The chemistry of friction surfaces and their state therefore determine their interaction with the lubricant components. However, this type of interaction, especially in industrial tribological systems, is very complex and difficult to explain, even applying the most modern analytical techniques.

Tribological test results (macroscopic effects) and molecular descriptions of a boundary layer are joined together in one dependence using the α_i model [16, 17]. The model is based on the application of system analysis to tribological systems. The model's main assumption is that due to the relationship between two functions $f(y)$ and $\phi(y)$, describing tribological processes in a given test, the coefficient α_i can be treated as a property of the lubricant which is not connected with only one tribotest as follows:

$$\alpha_i = \frac{f(b) - f(a)}{\phi(b) - \phi(a)} \cdot \frac{\phi'(b)}{f'(b)} \qquad \text{(Eqn. 8.1)}$$

It was concluded that:

(i) α_i is a measure of a lubricant's potential to create a protective boundary layer
(ii) $f(y)$ and $\phi(y)$ describe two processes concerning the tested oil, such as the provided energy and the dissipated energy, or wear as a function of load measured using two different testers, etc. Other variables influencing the investigated process are the same
(iii) a is a value of y (test result) constant for a group of tested lubricants
(iv) b is a value of y (test result) obtained for a given lubricant

Equation (8.1) may be transformed as follows:

$$\alpha_i = (f(b) - f(a))\,A \qquad \text{(Eqn. 8.2)}$$

where

$$A = \frac{1}{\phi(b) - \phi(a)} \cdot \frac{\phi'(b)}{f'(b)} \qquad \text{(Eqn. 8.3)}$$

A is a measure of the influence of a lubricant's potential to create a protective boundary layer as the result of a tribological process. It was found that the A value should be constant for a given mechanism but when the mechanism of a tribological process changes, A values change as well. Mathematical analysis gives the conclusion that this is possible when A is a harmonic function of y, a thesis confirmed by different test results. The same relationship can be obtained using the vector description of a tribological process when α_i can be represented as a scalar product of vectors X, the system input, and Y, the system output:

$$\alpha_i = A_x X \qquad \text{(Eqn. 8.4)}$$

$$\alpha_i = A_y Y \qquad \text{(Eqn. 8.5)}$$

The coordinates of vector X may be the concentration of additives, viscosity of the lubricating oil, work done on the system or even results of another test carried out with the test lubricant. The coordinates of vector Y may be wear, coefficient of friction, temperature generated during friction, concentration of stable products on the friction surface and dissipated energy, etc. Vectors A_x and A_y describe the relationship between the lubricant's ability to create a boundary layer, $\alpha_{i,}$ and the conditions and results of the tribological process, X, Y. Coordinates of A_x are connected with a given tribological system and coordinates of A_y with the tested lubricant (additive). A_x coordinates are constant when one tester and one procedure are used to test different lubricants or additives. A_y coordinates are constant when different tests for the same group of lubricants or additives are used. The practical importance of the α_i method is evident. If changes are selected that have the same value of A, then the factor that produces the observed change can be regarded as independent of the nature of the lubricant tested, expressed by α_i. An identical value of the α_i coefficient should be obtained for a given lubricant in two different systems when the process in one system is similar to that in the other.

The α_i method permits a better understanding of the interactions observed between ZDDP (zinc dialkyldithiophosphates) additives and various mineral base oils [17]. This applies for the anti-wear (AW), extreme pressure (EP) and antioxidant functions of ZDDP. The viscosity of base oils was shown to be a factor controlling these relationships. The α_i method has also been found useful in showing the directions of the relationships. For the case when an observed change should be considered as a complex one, the influence of the tested medium on it may be expressed as a sum as follows:

$$\alpha_\Sigma = x_1\alpha_1 + x_2\alpha_2 + \cdots + x_n\alpha_n \qquad \text{(Eqn. 8.6)}$$

where α_n is the α_i coefficient related to the nth simple change and x_n is the balance related to this change. The α_i method enables an estimate of industrial lubricant properties in one system to be obtained on the basis of test results obtained in another system. It also permits a quantitative analysis of the influence of lubricant properties on the lubrication process. Hence this method provides an elucidation of experimental results obtained by means of selected tribological and/or chemical tests [17].

8.1.4 *A New Approach to Heterogeneous Catalysis Combined with Tribochemistry*

The α_i model can also be used to elaborate a way to better understanding of heterogeneous catalytic processes. A catalyst is a substance that increases the rate at which a chemical system reaches equilibrium, without being consumed in the process; catalysis is the phenomenon of the catalyst in action while the catalyst lowers the activation energy. The transition state along a reaction path is the point of maximum free energy, where bond making and bond breaking are balanced. As presented in the previous section, this model can be applied to tribological systems in which the mechanical work done can be treated as input and dissipated energy, predominantly heat, as output. The functional input–output relation may also be related to tribochemical reactions which are known to proceed much faster than thermochemical ones. On the other hand one may compare tribochemical reactions with heterogeneous catalytic reactions [18].

The kinetics of tribochemical reactions depends on the conditions of the tribological process and, as a result, it is necessary to find more than one function of the tribochemical reaction mechanism. For example, one function can be related to the mechanics of the tribological process, the second function to its chemical reactions. It was assumed that the relationship between those functions makes it possible to analyse the mechanism of tribological processes on a 'basic level'. Two functions have been taken into account: $f(y)$ and $\phi(y)$. It was assumed that in both functions y is the only state variable.

Threshold energy, usually called activation energy, E_a, introduced in 1889 by Arrhenius, is defined as the energy that must be overcome to initiate a chemical reaction. This barrier energy denotes the minimum energy needed for a specific chemical reaction to occur. It is the height of the potential barrier, demonstrating the difference between the potential energy of the reactants and of the products. The Arrhenius equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds. From this equation, the activation energy can be expressed as follows:

$$E_a = -RT \ln(k/A) \tag{Eqn. 8.7}$$

where A is the prefactor and R is the gas constant. Either increasing the temperature or decreasing E_a, eg through the use of a catalyst, will result in an increase in the rate of reaction. The Arrhenius equation describes the dependence of the rate constant k of chemical reactions on the temperature T (in K) and E_a as follows:

$$k = A \exp(-E_a/RT) \tag{Eqn. 8.8}$$

The mechanism of heterogeneous catalysis is still under discussion and the same is for tribocatalysis. Usually, the decreased activation energy is presented as an apparent activation energy, E_{app}. However, there is no clear theory which explains the mechanism of material's influence on the ratio of chemical reactions.

Most recently it has been hypothesized that for standard and catalysed heterogeneous reactions the same E_a (*real activation energy*) is needed to initiate reaction processes [19]. It is proposed that the mechanical work done on the solid material is accumulated in this material and then emitted as electrons and/or photons to the space within which reactions take place. The developed model includes the specific angle γ at which the reaction can be initiated, when e_γ equals some 3–5 eV. It was demonstrated that the energy emitted by surfaces as impulses may reach the value of E_a and the heterogeneous catalytic process starts. Analysis of the mathematical model in relation to empirical results of tribological processes leads to the conclusion resulting in a new idea of the mechanism of catalytic processes. The critical ratio of triboreactions depends on energy emission by the solid body; the energy emission distribution by the solid body/catalyst is controlled by the angle of emission as follows:

$$e_\gamma = e_0 \cos \gamma \qquad \text{(Eqn. 8.9)}$$

where γ is the function of the load, *P*, and depends on the stream of energy introduced into the tribological system; e_0 is the density of energy flux in the perpendicular direction to the solid body surface, as in Fig. 8.1.

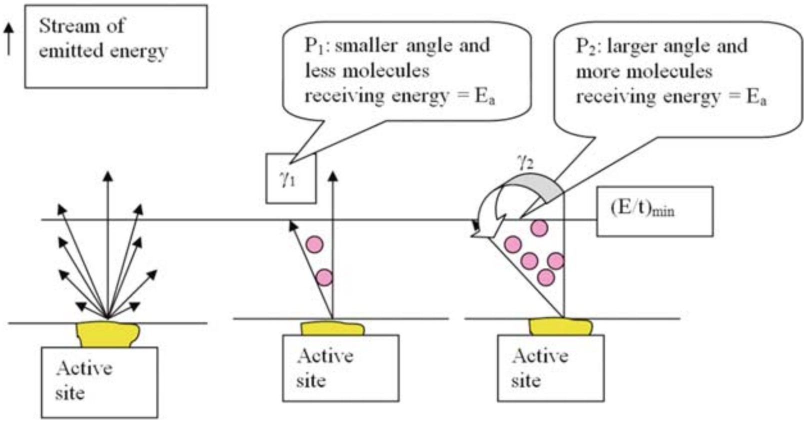


Fig. 8.1 Illustration of the main concept of the model; stream of the energy emitted by the catalyst, *E/t*, depends on the angle γ, hence the number of molecules receiving energy equal to E_a depends on γ [19]

The value of angle γ depends on the system energy flux. The critical state of the tribological system is in the destruction of the protective film. It has been observed that for different additives/reactants, the critical reaction rate leading to protective layer destruction was achieved for different values of energy flux into the system (different values of applied load *P*). The same value of *C* obtained for different additives/reactants and different densities of the stream of energy introduced into the system, which is characteristic of each additive/reactant, leads to the conclusion that the same critical rate of destruction reaction was achieved and consequently for each additive/reactant different angle γ is connected with the critical rate of reaction.

Consequently for each additive/reactant there is a specific value of the energy flux density, e_γ, emitted by the solid/catalyst and the value of activation energy E_a is constant. Accordingly, it is possible to state:

(i) E_a is constant for a given type of reaction and the critical rate of reaction depends not only on the energy quantity added to substrates but also on the density of the introduced energy stream (the time of tribological process is constant for each load)
(ii) the catalyst emits impulses of energy flux of high density and at an angle γ the value of energy emitted in a short time is equal to the activation energy, E_a
(iii) the catalyst collects energy introduced into the system and emits it as impulses of the high energy density flux, thereby initiating the reaction or increasing its rate.

In summary, it is possible to say that the activation energy, E_a, is constant for a given type of reaction and the reaction onset depends not only on the energy quantity added to substrates but also on density of the introduced energy stream. The catalyst emits impulses of energy flux of high density and at an angle γ the value of emitted energy is equal to the real activation energy, E_a.

8.2 Bearing Lubricants

8.2.1 Bearings

Bearings are the most important machine elements used in all branches of industrial machinery. They give smooth, low-friction, linear or rotary motion between two surfaces. Bearings function by a sliding or rolling action; those with sliding action are plain bearings, also ‘sleeve bearings, journal bearings’, whereas those with rolling actions are rolling-element bearings or antifriction bearings.

Bearings can be lubricated by gases, liquids, greases or solid lubricants; their main function is to keep the surfaces apart so that no physical interaction occurs and friction and wear are reduced. Bearings lubricated by gases include aerodynamic and aerostatic bearings with externally pressurized feed. Generally, for externally pressurized bearings the solid surfaces are separated by a fluid film supplied under pressure to the solid/solid interface. When the fluid is a liquid the lubrication mode is hydrostatic.

As plain bearing lubrication is more variable compared to that of rolling-element bearings, the former is also referred to according to the lubricating principle involved. Thus, a specific class of plain bearings is the full fluid film bearings which includes hydrodynamic, self-acting, and hydrostatic, pressurized feed bearings. For full fluid film bearings the load is supported by pressures within the separating fluid film and there is no contact between the solids. In the hydrodynamic lubrication the pressure is developed by the relative motion and the geometry of the system. The friction coefficient, f, in a plain bearing is related to the lubricant dynamic viscosity, η, the bearing load, W, and the sliding velocity, V, as follows:

$$f = k\left(\frac{\eta V}{W}\right) \tag{Eqn. 8.10}$$

This dimensionless term is known as the 'hydrodynamic factor', where Fig. 8.2 represents the Stribeck curve in the log scale and shows that a compromise must be made with respect to lubricant viscosity, between the friction losses in the region of hydrodynamic (HD) lubrication, and bearing wear when passing through the regime of mixed friction. Both hydrodynamic and hydrostatic bearings operate with infinite service life below some critical value of load and above a critical value of speed assuming other modes of wear such as corrosion and erosion are not experienced.

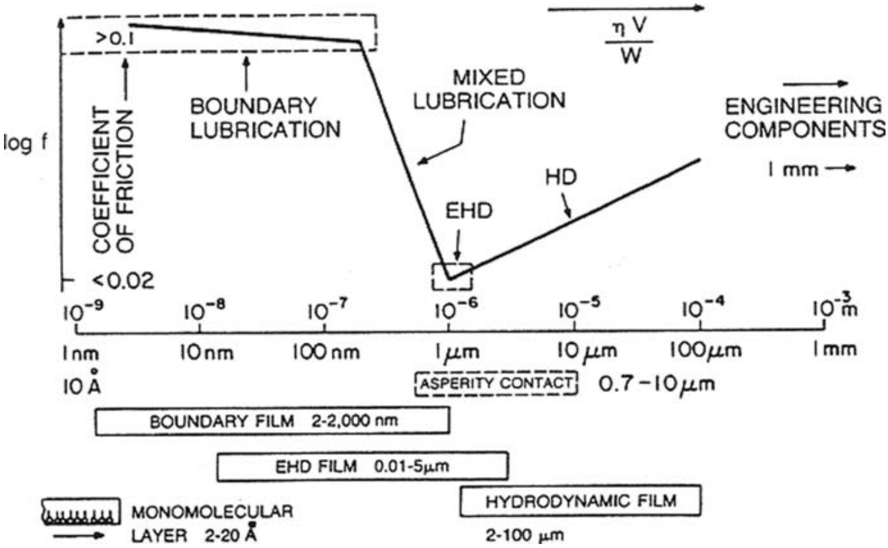


Fig. 8.2 Comparison of lubrication film thickness with the average size of lubricant molecules, redrawn and adapted from [6]

Another region of bearing lubrication is the elastohydrodynamic, EHD, lubrication which occurs naturally in rolling-element bearings and other high-contact-stress geometries such as gears and is a requirement for their successful operation. Two additional factors must be considered in this lubrication region, first that when a lubricant is squeezed under the advancing contact zone of a rolling element, it becomes more viscous, according to the following equation:

$$\eta_p = \eta_a \exp \alpha (p - p_a) \tag{Eqn. 8.11}$$

where η_p is the viscosity at pressure p, η_a is the viscosity at atmospheric pressure p_a and α is the pressure viscosity coefficient. This viscosity increase enables the lubricant to withstand the high contact stresses and inhibits contacts between the surfaces of mating elements. The other factor is that the contacting surfaces deform elastically, thereby enlarging the area of support and leading to more favourable lubrication. The friction coefficient for this lubrication region is the smallest, Fig. 8.2. Therefore, with EHD lubrication, the material properties of both the lubricant and the solids are important.

Mixed film conditions occur when a loss of the film resulting in momentary contact between the two surfaces is apparent. This occurs as a response to momentary variations in loading, called shock loading, that collapse the film and result in physical contact of opposing asperities [20].

Boundary lubrication in Fig. 8.2 is a specific condition of lubrication in which friction and wear between two solid surfaces in relative motion are mostly controlled by properties of the lubricant such as antifriction and load carrying, and also by the nature of the mating surfaces. Accordingly, boundary friction can be described as being determined by the properties of the solid surfaces and the lubricating properties of the lubricant, usually other than viscosity. The solid surfaces are rough and local contacts are established on asperity peaks. During the friction process the rough surfaces adhere to each other, generating clean surface spots which, in turn, interact with the environment to produce wear particles. Usually, application of mechanical energy associated with friction releases a great number of physical processes, Fig. 8.3, which causes tribochemical reactions of solids with molecules of lubricants.

The most important factor governing the tribochemical reactions under boundary friction is associated with the action of exoelectrons with lubricating oil components [21]. This is the basis of negative ion-radical action mechanisms, NIRAM. The general model of NIRAM assumes creation of two types of activated sites on friction surfaces, i.e. thermally activated sites and sites activated by exoelectron emission, EEE processes, Fig. 8.4. Comparison with thermally stressed solids and mechanically treated solids shows reactivity is often increased by several orders of magnitude, particularly in the low-temperature range.

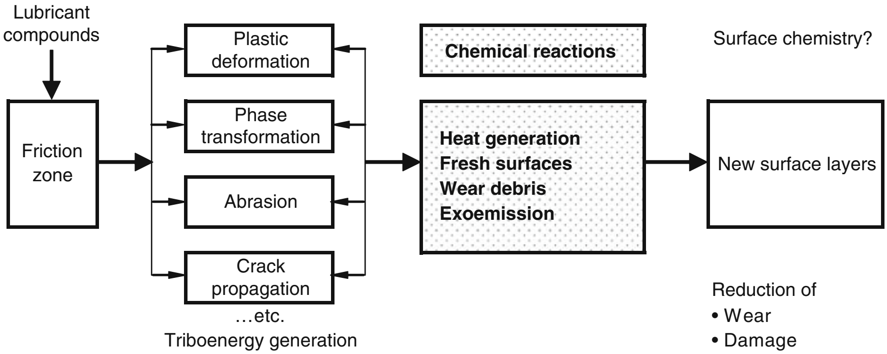


Fig. 8.3 Physical processes associated with surface enlargement during boundary friction, reproduced with permission from [21]

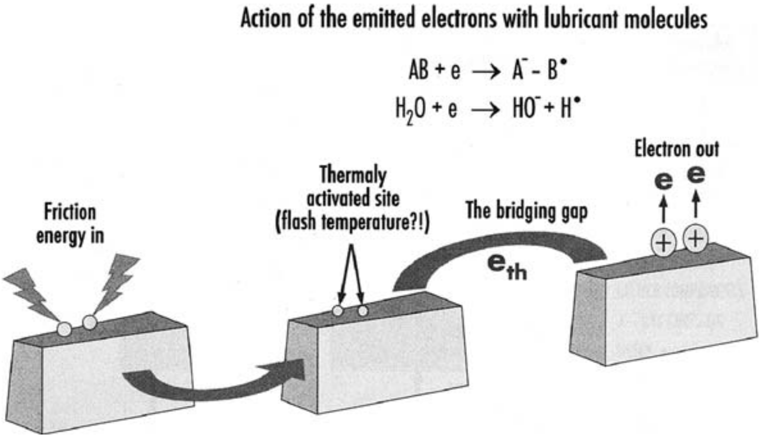


Fig. 8.4 Surface activation during friction [22]. *One of the factors controlling EEE is the work function, ϕ, of the solid

The individual lives of particles, as soon as they are formed from rough mating elements, are governed by mechanics, as far as velocity fields are concerned, and by materials science when composition changes are considered. The particles formed can be deposited in a very confined space, the contact, from which it is practically impossible for the particles to exit [23]. Each particle measures roughly 1 μm and the smallest contact width is at least 100 μm [24]. The trapped particles, which are usually highly active, separate the rubbing surfaces and alter the type of interactions that exist between the original solid surfaces, resulting in a significant effect on wear rates. For instance, mild wear particles interposed between rubbing surfaces are necessary for the severe–mild wear transition [25], such contact type relating to a third body approach, [26]. The term ‘third body’ refers to the material accumulated in a tribological contact, provided by either tangential or normal feed. The ‘third body’ can represent many phases piled up to form load-carrying areas and mostly includes amorphous material. In full contacts, in elastohydrodynamic (EHD) regions, the entire volume between first bodies, i.e. the machine elements, is filled with third bodies. Particles with chemisorbed lubricant components, or any other environmental component, can form an interface substance that fills up any pores or valleys and even up the sliding surfaces and, in turn, improves the friction process. As often found initially in the rubbing of hard materials, third bodies serve only as struts to separate first bodies [23]. An investigation of lubrication under water demonstrated that the frictional stress between two sliding surfaces bearing surfactant monolayers may decrease, when immersed in water, to as little as 1% or less of its value in air or oil [27]. This effect was attributed to the shift of the slip plane from between the surfactant layers to the surfactant/substrate interface.

Tribochemistry should also be combined with tribocatalysis, defined as:

> Tribocatalysis is the subsection of tribochemistry dealing with the changes of catalytic properties of solids due to the effect of mechanical energy [28].

Heterogeneous catalysis is activated when the catalyst slides against itself or other materials, e.g. ceramics. Oxidation reactions of hydrogen, carbon monoxide and methane were demonstrated as being enhanced by rubbing platinum, palladium and silver, respectively [29–31], and the reduction of carbon dioxide is enhanced by the rubbing of iron oxide [32].

8.2.2 Gaseous Lubricants

Gaseous lubricants belong to the simplest, lowest viscosity lubricants known and include air, nitrogen, oxygen and helium. They are applied in aerodynamic and aerostatic bearings. Since the chemical properties and the aggregate state of most gases remain unchanged over a wide temperature range, gaseous lubricants offer several advantages over liquid lubricants. First, they can be applied at both very high and very low temperatures. Their chemical stability eliminates any risk of contamination of the bearing by the lubricant, important for the machinery used in many branches of industry, primarily in the food, pharmaceutical and electronic industries.

A useful property of gases is that their viscosities increase with temperature, whereas the opposite is true of liquids, resulting in the load-carrying capacity of gas-lubricated bearings increasing with increasing temperature. However, the relatively low viscosity of gases generally limits the load-carrying capacity of self-acting, aerodynamic bearings to 15–20 kPa. It is possible to achieve better bearing performance with gaseous lubricants than with liquid lubricants due to the very low viscosity of the gases which results in smaller heat generation by internal friction. In some cases, such as in foil air bearings, sliding contact occurs during stops and starts [33], therefore solid lubricants such as PTFE are used to reduce friction.

8.2.3 Liquid Lubricants

Mineral oils: As the hydrodynamic behaviour of plain bearings is totally dependent on the viscosity characteristics of the lubricant, typical liquid bearing lubricants are straight mineral oil raffinates of various viscosity grades. The viscosity grade required is dependent upon bearing speed, oil temperature and load. Table 8.3 provides a general guideline to selecting the correct ISO viscosity grade [34]. The ISO grade number indicated is the preferred grade for the speed and temperature range. ISO 68- and 100-grade oils are commonly used in indoor, heated applications, with 32-grade oils being used for high-speed, 10,000 rpm, units and some outdoor low-temperature applications. The higher the bearing speed, the lower the oil viscosity required and also that the higher the unit operating temperature, the higher the oil viscosity required. If vibration or minor shock loading is possible, a higher grade of oil than the one indicated in Table 8.3 should be considered.

Table 8.3 Plain bearing ISO viscosity grade selection [34]

	Bearing/oil temperature (°C)			
Bearing speed (rpm)	0–50	60	75	90
300–1,500	–	68	100–150	–
~1,800	32	32–46	68–100	100
~3,600	32	32	46–68	68–100
~10,000	32	32	32	32–46

Other methods [35] for determining the viscosity grade required in an application are to apply minimum and optimum viscosity criteria to a viscosity–temperature plot. A third and more complex method is to calculate the oil viscosity needed to obtain a satisfactory oil film thickness.

The lubrication of bearings for machine tools usually requires mineral oils of ISO VG 46 or 68. For fast-running grinding spindles with plain bearings, mineral oils of ISO VG 5 or 7 are required, dependent on bearing clearance and speed. Bearings operating under high loads need lubricants of ISO VG 68 or 100. The service life of the bearing can be increased if the viscosity of the selected liquid lubricant at operating temperature exceeds the calculated optimum viscosity.

On the other hand, increased viscosity also increases operating temperature. In practice, therefore, the extent to which lubrication can be improved in this way is often limited. The chemical compositions of these oils differ from typical base oils in that they contain somewhat more aromatic hydrocarbons and heterocyclic compounds, which act as natural oxidation inhibitors. An increased viscosity for oils derived from the same crude oil does not significantly change their chemical composition, the difference generally lies with the increasing chain length of the paraffinic hydrocarbons, mostly isoparaffins, and in the aliphatic substituents of naphthenic and aromatic rings, together with a slight increase in the number of naphthenic and aromatic rings. More highly refined mineral oils and oxidation inhibitors are used for applications where higher temperatures or longer service periods require better ageing stabilities.

Tribological additives are required for bearings which operate with frequent changes in the sliding or rotation direction, or with frequent stops and start. When metal-to-metal contact is imminent, a lubricant's ability to prevent catastrophic wear or damage depends on the effectiveness of anti-wear and/or extreme pressure additives. Three groups of additives are important, namely anti-wear, extreme pressure additives and friction-reducing agents. It is important to remember that in many cases bearings are lubricated as part of the overall lubrication system requirement for a given piece of equipment, e.g. engine oils, compressor oils, gear oils. Other additives that may be included are rust and oxidation inhibitors, anti-foam and pour-point depressant additives.

It should be recognized that using lubricating oils of higher viscosity to ensure satisfactory lubrication causes increased energy demands due to high internal friction.

Synthetic oils: In practice, every synthetic oil of adequate viscosity and good viscosity–temperature behaviour can be used as a bearing lubricant, e.g. polyglycols are very good bearing lubricants for mills and calenders in the rubber, plastics, textile and paper industries. However, in most cases the synthetic oils specifically developed for lubricating particular equipment are also used to lubricate its bearings. Although synthetic lubricant viscosities change slowly with temperature, some synthetic oils do not form a lubricant film under pressure as well as mineral oils and may not be effective bearing lubricants despite their higher temperature viscosity [36].

Biodegradable products: Biodegradable products of vegetable or animal origin are also considered for liquid lubrication, e.g. the effects of sunflower oil added to base oil on the performance of journal bearings [37]. The use of vegetable oils as lubricants is likely to increase due to environmental and government requirements and is becoming increasingly important.

Cryogenic fluids: Specific cryogenic fluids such as liquid oxygen, hydrogen and nitrogen are another group of liquid bearing lubricants, used in aerospace applications. It is usual that bearings operating in these fluids are sufficiently cooled, but not sufficiently lubricated, by them, due to their very low viscosities.

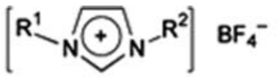
Ionic liquids as lubricants for porous bearings: Sintered metal self-lubricating bearings, based on powder-metallurgy technology, are economical, suitable for high production rates and can be manufactured to precision tolerances [38]. Porous metal parts usually consist of compacted metal powder of either bronze or iron with interconnecting pores of up to 10–35% of total volume. During operation, lubricating oil is stored in the voids and feeds through the interconnected pores to the bearing/axle tribocontact.

Porous metal parts, characterized by an open-porous structure, can store oil up to 15–25% of total bearing volume. Any oil forced from the loaded zone of the bearing is resorbed by capillary action. Various material combinations can meet specific lubricant requirements for such bearing types, e.g. 1–3.5% graphite is frequently added to the bearing sinter powder to enhance self-lubricating properties. The load-carrying capability of the materials used is carefully assessed and selected, thus a material usually of high porosity with a maximum amount of lubricating oil is used for high-speed/light-load applications. A low-oil-content/low-porosity material with high graphite content is more satisfactory for oscillating and reciprocating motions where it is difficult to build up an oil film. As these bearings can operate for long periods without additional lubricant supply, they are used for life-time lubrication and in inaccessible or inconvenient places where relubrication would be difficult. Sintered-metal self-lubricating bearings are widely used in home appliances, small motors, machine tools, aircraft and automotive accessories, business machines, instruments and farm and construction equipment. In automobiles they are particularly usefully installed in numerous secondary units such as drives for electrical windows, fans, windscreen wipers.

Experiments determined the effect of lubricant selection and lubricating conditions on the tribological characteristics of porous bearings [39], using pure base oil, two fully formulated commercial engine oils and a few lubricating oils with commercial additives. Examination of the worn surfaces of test bearings using optical microscopy and experimental results showed that the friction coefficient was more stable and lower under static loading than periodic loading. Friction coefficients and wear rates conducted with base oil alone resulted in higher values than those of fully formulated oils with, and without, a special component. The study indicated that the accurate selection of lubricant and suitable running conditions are very important for the tribological characteristics of porous bearings. Most recently ionic liquids have been considered as lubricants for porous bearings.

Ionic liquids are materials composed only of ions, either negatively or positively charged atoms or groups of atoms. Some ionic liquids are in a dynamic equilibrium where at any time more than 99.99% of the liquid consists of ionic rather than molecular species. In the broad sense, the term includes all molten salts at temperatures higher than 800°C, the melting point for common salt, NaCl. The term 'ionic liquid' is commonly used for salts whose melting point is relatively low, below 100°C, achieved by the composition of organic ions, in particular cations.

Ionic liquids have a number of properties that suggest they may have high potential as lubricants for special applications. Most ionic liquids have very low combustibility, excellent thermal and hydrolytic stability, a wide liquid range and favourable solvating properties for diverse compounds. Their miscibility with water or organic solvents varies with choice of anion and cation together with side chain lengths on the cation. Thermal stabilities and melting points significantly depend on the components of the ionic liquid. Potential technological applications of ionic liquids are broad, for example, use as high- and low-temperature lubricants. Ionic liquids consist of bulky and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium and organic ammonium ions. A wide range of anions is employed, from simple halides to inorganic anions such as tetrafluoroborate and hexafluorophosphate and to large organic anions like bis-trifluorosulphonimide. It is anticipated that ionic liquids such as alkylimidazolium tetrafluoroborates L106 and L206, depicted below, Fig. 8.5, could be promising versatile lubricants for the contact of steel/steel, steel/aluminium, steel/copper, steel/SiO_2, Si_3N_4/SiO_2, steel/Si(100), steel/sialon ceramics and Si_3N_4/sialon ceramics [40–42]. These ionic liquids compared with two fluorine-containing lubricants, phosphazene [43] and perfluoropolyether [44], gave reduced friction coefficients. And, in some cases reduced wear. They gave the tribological system investigated high load-carrying capacity. In addition, the ionic liquids L106 and L206 have prominent low-temperature fluidity (pour points below −55°C), high-temperature stability and low vapour pressure making them an attractive alternative to conventional liquid lubricants. Other ionic liquids, such as alkylimidazolium hexafluorophosphates, are also being investigated as potential lubricants in high-performance applications for steel/steel contacts [45].



L106: $R^1 = CH_3$ $R^2 = n\text{-}C_6H_{13}$

L206: $R^1 = C_2H_5$ $R^2 = n\text{-}C_6H_{13}$

Fig. 8.5 Structure of a typical ionic liquid

The potential application of ionic liquids in porous metal bearings was recently investigated in detail for physico-chemical and tribological properties [46]. Tribological performances of selected commercially available ionic liquids and reference lubricants for different porous metal bearing types were evaluated using a precision-bearing tribometer. Stribeck curves were obtained which proved that ionic liquids showed at least equal behaviour compared with conventional reference oils in terms of hydrodynamic friction coefficient and the speed at which the boundary to hydrodynamic lubrication transition appeared. Experiments relating to physico-chemical properties focussed on rheological properties, thermal–oxidative stability and corrosiveness. Some ionic liquids showed satisfactory viscometric properties over the entire temperature range investigated from –40 to 100°C. Variation in thermal–oxidative stability could be related to molecular structure. The corrosiveness of ionic liquids considerably depended on molecular structure, the metal being lubricated and the temperature. In contrast to copper-containing materials, iron-based materials were hardly affected by exposure to ionic liquids.

A complementary study of steel/steel contacts (100Cr6) [47] used an oscillation wear and friction tester to screen ionic liquids in the boundary lubrication regime at 30, 100 and 170°C at 200 N load. Results are summarized as follows: (i) some promising ionic liquids gave lower friction and wear at all temperatures, compared to reference lubricants, (ii) chemical structures of ionic liquids have a high impact on their physico-chemical as well as on tribological properties and (iii) careful selection of both cation and anion, as a tailor-made ionic liquid, enables adaptation of ionic liquid structures to specific applications.

Recent work: Semi-lubricated journal bearings consisting of a shaft rotating in a porous metal sleeve of sintered bronze or aluminium containing lubricating oil within the pores of the porous metal are restricted to low loads, low-to-medium velocity and temperatures up to 100°C [48].

Extremely low friction is achieved by using a divergent, pre-contact 'surface force' – the repulsive, so-called 'van der Waals force' [49]. In almost all cases this force is attractive but for certain material combinations it is manifestly repulsive. At short separations, of the order of molecular distances, the load-bearing capacity provided by the repulsive force is large. This clearly shows that two surfaces experiencing repulsive surface forces and which diverge at small separations can slide essentially without friction. The number of systems where repulsive van der Waals forces could occur is limited but includes metal bearings in a PTFE housing with organic lubricant and also certain combinations of technically interesting ceramic materials. Recent proposals include enhancing van der Waals forces by microwave and visible ranges of electromagnetic radiation further open up the possibility of achieving friction-free sliding in a much wider range of systems.

Film lubrication has the general assumption that the liquid layer directly in contact with a solid surface moves at the same speed as the surface itself. However, recent work has shown that simple liquids can slip against very smooth, lyophobic surfaces including monolayer-coated mica, sapphire and silicon [50]. Liquid slip was believed to cause (i) a significantly reduced hydrodynamic squeeze force in lubricated ball-on-flat and crossed cylinder contacts when one or both surfaces are made lyophobic, (ii) reduced Couette shear force in a reciprocating, ball-on-flat geometry when one surface is lyophobic and (iii) contrasting velocity profiles measured next to lyophobic and lyophilic surfaces using fluorescent particles and fluorescence recovery. It was shown that lubricant-type liquids including hydrocarbons, silicone oils and water can slip very easily against surfaces which are lyophobic with rms surface roughness <6 nm. These results may be of great importance in understanding bearing lubrication as well as in developing new lubrication technologies.

8.2.4 Greases

Greases are almost universally used to lubricate ball- and roller-element bearings and widely applied in rolling element bearings in machine tools, electric motors, household appliances and many others. For adequate consistency and high dropping point, thickening agents such as lithium or sodium soaps and mixed calcium and sodium soaps are used, for more details, see Chapter 14. Bearings are normally lubricated with greases of the consistency grades: 1 (soft), 2 (creamy) and 3 (almost solid), selected according to speed, bearing sealing, position of the bearing, working temperature, starting torque, etc. These lubricants must prevent rusting under wet conditions and the catalytic effects of metals and are characterized by good oxidation stability. It is essential that a greased bearing is protected against the environment such that no moisture or impurities can penetrate the assembly. Sealing also acts to prevent grease from leaking out.

Sodium petroleum sulphonates or calcium dinonylnaphthalene sulphonate can be applied as rust preventing additives and the catalytic effect of copper can be retarded by 2-mercaptobenzothiazole. Depending on operating temperature, various oxidation inhibitors may be used. Thus, 2,6-di-*tert*-butyl-4-methyl phenol is an effective inhibitor below 120°C while phenyl-alpha-naphthylamine is widely used in greases at low temperatures and above 120°C and phenothiazine is effective especially at temperatures above 150°C. Special compounds used as oxidation inhibitors for greases in the food industry are dilauryl thiodipropionate or citric acid.

Another class of additives proposed for bearing greases is metal or metal alloy nanoparticles that are more anodic than the material of which the inner or outer raceways of ball and rolling element bearings are constructed [51]. These additives are suspended in the lubricant and movement of the rolling elements on the raceways within the bearing forms a film from the nanoparticles.

Fluorocarbon polymers can be used as thickeners in grease formulations, making use of their excellent temperature stability, lubricating properties and chemical inertness. The next step is to use perfluoropolyether/polytetrafluoroethylene, PFPE/PTFE, grease in the high-temperature operating environment of heated roll bearings [52], where PFPE oils, thickened into a grease with PTFE, provide superior wear protection in this application. PFPE withstands high temperatures, hostile chemicals and volatile atmospheres for, unlike hydrocarbons that begin to degrade at 100°C, PFPE is chemically stable to 343°C. It will not burn, does not react with oxygen when it does begin to break down and the breakdown products vaporize to leave no gummy tars or deposits. PFPE grease forms its own seal around the bearings and resists common solvents and long-term contact with steam and boiling water. Being about twice as dense as the typical hydrocarbon lubricant, PFPE has superior load-carrying capability and film-forming characteristics which are critical factors in extending the operating life of a bearing.

It was thought that current generations of biodegradable and low-toxicity lubricants could not satisfactorily meet the requirements of rolling element bearings. Recently, a new biodegradable grease was demonstrated based on synthetic ester oil, a lithium/calcium thickener and other biodegradable ingredients which can be used in bearing applications [53].

Plain bearings are normally oil lubricated but they may also be grease lubricated for slow-speed equipment where cooling of the bearing is not a factor, particularly if subject to frequent starts, stops or reversing, if shock loading occurs or may be physically difficult to reach [20, 34]. Grease selection begins with consideration of the oil to be used; after the proper viscosity oil has been selected, then the soap thickener, oxidation and rust characteristics, worked consistency properties, pumpability for automatic systems and load bearing, EP/AW, properties are considered. For long intervals and very heavy loading, solid additives such as molybdenum disulphide or graphite may be incorporated. The solid additives serve to mechanically prevent metal contact in mixed film and boundary lubrication conditions.

8.2.5 Solid Lubricants

General description: Bearings used under vacuum, at very high temperatures or under very high radiation cannot be lubricated by liquid lubricants or greases. For these and many other cases, solid lubricants are used, deemed to be any solid material used to reduce friction and wear between two moving surfaces.

In general, the solid material is interposed as a film between sliding and/or rolling surfaces. Simply stated, an adequate solid material is required for the special lubrication requirements of extreme operating conditions, such as very high or very low temperatures over a wide range, e.g. –200 to 850°C, and corrosive atmospheres. Such materials normally have a layered crystalline structure which ensures low shear strength, thereby minimizing friction. The shear strength between the crystalline layers is weak and sets up a low friction mechanism by slippage of the crystalline layers under low shearing forces [54]. Examples of layer-lattice solids are molybdenum disulphide, graphite, boron nitride, cadmium iodide and borax. Solid lubricants are used mainly in the form of powders or as bonded solid films.

A good solid film lubricant has strong adhesion to the bearing substrate material, full surface coverage and good malleability. It should also be chemically stable and prevent corrosion, taking into account operational and environmental conditions. Many solid film lubricants have poor wear resistance, since any breaks in the film are not self-healing, in contrast to the surface coating formed by a liquid lubricant. Advanced solid film lubricants perform reliably in many specific applications and much experience has been gained to better understand their limitations. The most commonly used solid lubricants encompass four materials: molybdenum disulphide, graphite, polytetrafluoroethylene and polyfluoroethylene propylene [54].

Another group of materials, the self-lubricated materials, are related to solid lubricants and are particularly important for bearings. Their self-lubricating characteristics eliminate the need for grease or other lubrication and give improved performance under high-temperature conditions. Graphalloy (graphite/metal) alloys make use of the special properties of graphite, the structure of which can be compared to a deck of cards with individual layers able to easily slide off [55]. This phenomenon gives the material a self-lubricating ability matched by few other materials and allows for the elimination of grease or oil that would evaporate, congeal or solidify, causing premature failure. The graphite matrix can be filled with a variety of embedded lubricants to enhance chemical, mechanical and tribological properties to give a constant, low friction coefficient rather than just a surface layer, helping to protect against catastrophic failure. Lubrication is maintained during linear motion where lubricant is not drawn out and dust is not pulled in.

A recent development in solid bearing lubricants is microporous polymeric lubricants, MPL, where a polymer containing a continuous microporous network has oil contained within the pores, which may include appropriate additives [56]. The oil content in the polymer can be more than 50% by weight and the microporous polymer acts as a sponge, releasing and absorbing oil when necessary.

Solid lubricant powders in non-bonded films: Solid lubricants in powder form are primarily tribological additives used in pastes, greases and suspensions. Molybdenum disulphide and graphite pastes are used for highly loaded journal and rolling bearings as well as for ball joint pivots and normally contain high concentrations, 20–50%, of the solid lubricant. As molybdenum disulphide can reduce oxidation resistance of the carrier lubricant, oxidation-resistant mineral oils and polyalkylene glycols are used as the liquid components, silicone oils are used at higher temperatures. Molybdenum disulphide gives increased load-carrying capacity and improved boundary friction properties when added to most greases but on the other hand it can reduce both oxidation resistance and corrosion resistance. This negative effect can be largely overcome by adding suitable inhibitors. Addition of molybdenum disulphide to a grease provides increased grease life in selected, but not all, applications. For example, it has been found that non-molybdenum disulphide containing greases gave longer service lives in airplane flap track needle bearings than greases containing 5% molybdenum disulphide [54]. Fluorocarbon polymers such as polytetrafluoroethylene and polyfluoroethylene propylene ensure low friction on wearing surfaces when added to greases.

Surface modification of nanoparticles in some cases allow the formation of stable dispersions in liquid hydrocarbons [57]. If molybdenum sulphide nanoparticles are considered as friction-modifying additives for liquid lubricants, then a whole range of new possibilities appears. The action of tribologically active additives as nanoparticles has been proposed as in Fig. 8.6.

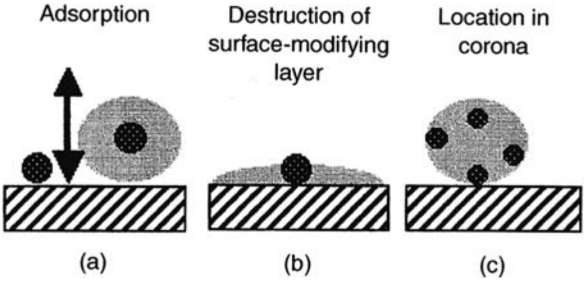


Fig. 8.6 Mechanism of action of tribologically active additives in nanoparticle form: **(a)** adsorption step for 'molecular' and 'nanoparticulate' species; **(b)** destruction of the surface-modifying layer; and **(c)** several nanoparticles in a polymeric micelle [57]

Suspensions of solid lubricants are used as a colloidal or partially colloidal dispersion, in mineral oils, polyglycols or silicone oils as carrier liquids. These suspensions are used to impregnate sintered bearings or added to running-in oils for bearings.

The most important advantage of solid lubricants used as a thin film burnished onto wearing surfaces is to give low friction. Molybdenum disulphide in powder form is more effective than graphite. Application of graphite is very limited because of galvanic corrosion problems and high friction characteristics under vacuum. Burnished films are also used as a break-in lubricant for shafts, rollers and constructional elements of ball bearings with the advantage that they generate a minimum amount of debris. Thus, burnished films are used for close tolerance bearings.

Bonded solid films: Bonded solid film lubricants are a combination of solid lubricant powder dispersed in an adhesive binder and diluted with solvent. This formulation allows application by spraying, dipping or brushing to form a film. Such films are often described as 'lubricating paints' where the pigment is substituted by a solid lubricant called the lubricant pigment. Among the organic binders, thermosetting resins such as phenolic, epoxy, acrylic, alkyd, silicone, vinyl and polyurethane resins are used. Polyimides, water glass and ceramics such as Al_3PO_4 are used at higher temperatures. Another group includes thermoplastic materials such as nylon, acetal copolymers or PTFE [58]. These bearings usually consist of a thin layer of bearing material bonded onto a metal backing, e.g. bearings such as SKF GLYCODUR F and Glacier DU consist of a steel backing and a sintered bronze layer. The porous bronze is filled with PTFE and other friction-reducing additives. Thermoplastic bearing materials can be filled with glass, carbon, bronze or lead. Metals such as silver, lead or gold are also used alone as bonded solid films. Bonded solid film lubricants can give low friction operating in extreme environments of temperature, pressure and vacuum. Furthermore, they can prevent adhesion and wear between mating elements, require little or no maintenance and can simplify the design of bearings. Bonded solid film lubricants are preferably used for sliding surfaces subjected to high loads and low sliding speeds. Hence they are often used in journal bearings where the required wear life is within the capability of the film and where weight and space considerations are critical.

The general limitations of bonded solid film lubricants may be summarized as follows: (i) they do not last indefinitely, (ii) possibly promoting corrosion and are not corrosion preventive coatings, (iii) they have no capacity to remove frictional heat, (iv) in most cases, re-lubrication is not possible, (v) application techniques and surface preparation must be meticulously controlled or performance is jeopardized and (vi) inspection techniques are not always satisfactory [54].

Molybdenum disulphide bonded films alone or in combination with antimony trioxide, Sb_2O_3, zinc oxide, ZnO, or tantalum disulphide, TaS_2, are suited for low sliding speeds at high loads. Although bonded solid films are widely applied in many areas, their limited wear life together with other limitations which affect their performance restrict their range of applications. For bonded films containing molybdenum disulphide, graphite and antimony-thioantimonate, $Sb(SbS_4)$, as single, two- or three-component systems, the optimum formulations of MoS_2/graphite, $MoS_2/Sb(SbS_4)$ or MoS_2/graphite/$Sb(SbS_4)$ gave a longer wear life than each component alone [59]. $Sb(SbS_4)$, which has no lubricating properties whatsoever, improves the tribological behaviour of molybdenum disulphide and graphite.

An inorganic solid lubricant has been described as a self-lubricating composite comprising a chromium oxide (e.g. chromic oxide, Cr_2O_3), a metal binder comprising Cr/Ni or Cr/Co alloy, a metal fluoride, and, optionally, a metal lubricant [60]. A milled powder mix of the composite is deposited onto a substrate, e.g. by plasma spraying.

Another kind of inorganic solid lubricant coating consists of:

- a bonding component, such as silver sulphide/copper sulphide, silver sulphide/lead sulphide, silver sulphide/bismuth sulphide, nickel oxide/vanadium pentoxide and calcium fluoride/magnesium fluoride
- a wear-resistant component such as nickel oxide, aluminium oxide, chromic oxide and barium oxide
- a friction-lowering component such as metal sulphides, metal fluorides or precious metals such as gold, silver, platinum and the like
- and, optionally, a polymer binder such as ethyl cellulose or nitrocellulose and a solvent such as terpineol or pine oil [61]

Another material of this kind is tungsten disulphide, originally developed by NASA for aerospace applications, now also applicable to specialty industries [58]. Ti_3SiC_2 is a thermodynamically stable, nano-layered, ternary carbide and part of a family of over 50 ternary carbides and nitrides, the ‘MAX phases’ [62]. These phases are a new class of solids possessing unique combinations of properties: they are readily machinable, relatively soft for ceramics, but elastically stiff, and electrically and thermally conductive. They combine the good properties of both metals and ceramics that could lead to this technology contributing to future lubricant developments.

8.3 Compressor Lubricants

8.3.1 General Description

Compressors are widely used in industry for compressing many types of gases to store and/or transport them, either as compressed gas or as liquids. There are three main types of compressors, namely reciprocating, rotary and turbo-type air compressors. Reciprocating compressors employ a piston and cylinder with valves. Rotary compressors are further divided into either sliding vane or screw, the former traps gas in a succession of cells, the latter compresses gas between intermeshing screws. Both types bring lubricant and gas into intimate contact over a large area of exposed surfaces under high pressure and high temperature, such conditions promoting chemical reactions. Consequently, when compressing air, lubricants with excellent oxidative stability must be used. Turbo-type air compressors operate continuously by increasing gas velocity and the lubricant does not come into contact with the compressed air, therefore the requirements are less severe.

The three main groups of compressor lubricants are for (i) gases, (ii) refrigerators and (iii) vacuum pumps. Depending on the application, various classes of lubricating oils are used, including mineral oils of various levels of refinement, semi-synthetic and/or synthetic oils. Some lubricants for gas compressors may contain a wide variety of additives.

8.3.2 Lubricants for Gas Compressors

There is a wide range of compressor oils with viscosities ranging from about $4\,\mathrm{mm^2/s}$ at 100°C to over $20\,\mathrm{mm^2/s}$ at 100°C, covering ISO VG 22, 46, 100, 150 and 460. Criteria for selecting the lubricant depend primarily on the gas to be compressed and the design of the compressor which determines the final compression temperature.

The purpose of the oil in the pressurized section of the compressor is to reduce friction, prevent wear, improve sealing of the pressurized spaces and provide cooling. Some functional similarities are readily found between air compressor oils and engine oils in certain types of compressor oil, clearly recognized since heavy duty oils of appropriate viscosities are used to lubricate mobile compressor units on vehicles or in workshops. The lubrication of the pressurized section is difficult, particularly when oxidizing/aggressive gases are present due to the significant safety hazard involved.

Air is the most frequently compressed gas and lubricants for reciprocating air compressors have low carbon-forming tendencies because carbonaceous deposit formation in the air discharge system is the prime cause of fires and explosions. The fire and explosion risk is usually controlled by selection of good quality petroleum-based lubricants. Fire-resistant halogenated fluids are used as compressor lubricants for oxygen compressors. The higher the final compression, the higher the air outlet temperature and correspondingly, higher requirements for oxidative stability of the lubricant and its resistance to sludge formation. Oxidation processes under pressure may be catalysed by finely dispersed iron oxide which also lowers the lubricant ignition temperature.

Gas compressor lubricants based on mineral oils contain (i) oxidation inhibitors to prevent varnish and sludge formation and retard corrosion of alloy bearings, (ii) rust inhibitors, (iii) polar compounds to improve lubrication in the presence of water and (iv) anti-wear and anti-foam agents. Gas compressor lubricants of the highest requirements are made from specially selected, highly refined base oils with a low coking tendency and an appropriate additive package, including a corrosion inhibitor. Thus, the chemistry of gas compressor lubricants exhibits a considerable similarity to that of engine oils.

Synthetic oils are widely used as gas compressor lubricants. Polyalkylene glycols are used for the compression of hydrocarbon gases, e.g. refinery gases and natural gas. Table 8.4 shows oil selection for natural gas compressors, dependent on discharge pressures. The application of this synthetic lubricant prevents a viscosity drop in the pressurized section and washing away of the lubricant which may cause dry running. Polyalkylene glycols are adequate lubricants for compression temperatures up to 200°C without forming any kind of deposits in service. Other synthetic gas compressor lubricants include (i) diesters and polyesters, (ii) polyalphaolefins and (iii) dimethyl silicones and fluorinated silicones. These synthetics, along with polyalkylene glycols, are most widely used since they meet the requirements for most compressor applications.

For long-term hydrolytic stability and exceptional water separation, polyalphaolefins are the preferred rotary compressor lubricants. The energy cost savings

Table 8.4 Compressor lubricant product selection variations [48]

Discharge pressure (psi)	Pipeline or sales gas (sweet, dry natural gas)	Raw natural gas (wet) water or HC liquids or sour/acid (H_2S)	Solvent gas – raw natural gas with high CO_2 level or propane refrigerant
<1200	NGEO, SAE 40 ISO 150	Reciprocating natural gas compressor cylinder oil, mineral ISO 220	Reciprocating natural gas compressor cylinder oil, mineral ISO 220
1200–2500	Reciprocating natural gas compressor cylinder oil, mineral ISO 220	Reciprocating natural gas compressor cylinder oil, mineral ISO 220–320	Reciprocating natural gas compressor cylinder oil, mineral ISO 320–460 or PAG synthetic, 150–220
2500–4000	Reciprocating natural gas compressor cylinder oil, mineral ISO 220–460	Reciprocating natural gas compressor cylinder oil, mineral ISO 320–460	PAG synthetic, ISO 150–220
>4000	PAG synthetic, ISO 150–220	PAG synthetic, ISO 150–220	PAG synthetic, ISO 150–220

achieved by conversion to polyalphaolefin lubricant give a 9-month payback for the extra cost of the lubricant [63], additional benefits included longer lubricant change intervals, extended oil filter life, extended overhaul intervals and less downtime. Polyalphaolefin lubricants are used together with additives specifically formulated to increase chemical stability, thermal stability and to reduce corrosion and are increasingly accepted for use with ammonia gas.

8.3.3 Lubricants for Refrigerators

Compared with lubricants for gas compressors, lubricants for refrigerators have lower viscosities, ISO VG ranging from 15 to 100. Characteristic features of these lubricants are good low-temperature properties and compatibility with the refrigerant. Lubricants for refrigerators are widely employed in cold storage plants and ships; furthermore, they are used in sealed refrigerators and air conditioners with lifetime refrigerant charges. Ammonia is used as a refrigerant in large plants and another group of refrigerants are the fluoro- and chlorofluorohydrocarbons, HCFCs, which, unlike ammonia, are oil miscible. Chlorofluorocarbons, the CFCs, are now almost completely phased out.

Refrigerating compressors operate with the exclusion of air; therefore, lubricant oxidation is low and consequently refrigerator lubricants are generally free of additives. The absence of additives removes the possibility of additive degradation products reacting with the refrigerant.

Highly refined naphthenic base oils are used for low pour-point temperatures. Paraffinic base oils must be thoroughly de-waxed, otherwise solids will precipitate in the cold halogenated hydrocarbons when the lubricant is diluted with refrigerant at a temperature below the cloud point of the lubricant. The solids will plug control devices and lines of the refrigerating plant and affect heat exchange. Although some refrigeration systems use immiscible systems, the lubricant is usually required to have good miscibility with the refrigerant, thus it is an important property of a refrigerator lubricant and controlled by both the chemistry and viscosity of the lubricant. Paraffinic oils are less miscible in the cold than are naphthenic or aromatic oils [7]; however, the chemical stability of highly aromatic oils is lower and only sufficient in exceptional cases. In consequence, high viscosity index, HVI, isoparaffinic hydrocarbons are increasingly used as lubricants for refrigerators. While their immiscibility increases with increasing viscosity, this effect is less pronounced than that due to the chemistry of the lubricants.

Semisynthetic oils, as mixtures of mineral oils and synthetic alkylbenzenes, or pure synthetic alkylaromatics are good refrigerator lubricants with good thermal stabilities, low pour point and favourable miscibility properties with refrigerants. Semisynthetic and synthetic refrigerator lubricants are especially suitable for refrigerator systems operating at very low evaporator temperatures where ‘Refrigerant 22’ is used.

The refrigeration industry has shown interest in using carbon dioxide as a refrigerant in some applications because it is environmentally friendly, non-flammable, non-toxic and an economical alternative to harmful hydrofluorocarbon refrigerants, HFCs. Scuffing inside the compressor in high-pressure carbon dioxide systems remains a major concern. The effect of carbon dioxide on the tribological behaviour of contact surfaces at realistically higher pressures up to 6.9 MPa found that for all cases a small amount of PAG lubricant (ISO VG 46) ensured boundary lubrication conditions [64]. Carbon dioxide at higher pressures has a positive effect on tribological performance, a very important step because tribological testing in the presence of carbon dioxide had not been undertaken before. It gives insights to the tribological behaviour of carbon dioxide at very high pressures.

8.3.4 Vacuum Pump Lubricants

Both the vacuum section and moving parts of vacuum pumps may be lubricated by the same lubricants as those used for gas compressors. This only applies to industrial equipment producing low or medium vacuum. For high vacuum, lubricants must have better properties, particularly vapour pressure and sealing of the vacuum section, therefore more viscous lubricants are used. The best petroleum-based vacuum pump lubricants are narrow oil fractions of sufficiently high viscosity. These oils have high flash points and do not contain low-boiling components which will affect the final vacuum achieved, produce oil mist and lead to condensate formation in adjacent areas.

To lubricate high and ultra-high vacuum pumps special lubricants with low vapour pressures at the working temperature are used, produced from naphthenic or paraffinic mineral oils by molecular distillation with good oxidative and thermal stability. Synthetic esters are another group of lubricants for vacuum pumps, the most widely used are di-*n*-butyl and di-*n*-octyl phthalates.

8.4 Hydraulic Lubricants (Fluids)

8.4.1 General Description

Hydraulic systems, i.e. hydraulic power transmission equipment, have a wide range of applications where multiplication of force is required or where reliable control gear must be provided. Developments in automation have significantly extended the use of hydraulic equipment. Typical hydraulic equipment consists of a circulating system comprising a pump, a series of control valves and hydraulic motors/actuators. The pump is the most critical lubricated component in the hydraulic system, usually being a sliding vane, piston or gear pump. Although lubricants for hydraulic systems must reduce friction and prevent wear of the mating elements, especially for pump components, in practice they are usually called hydraulic fluids.

Hydraulic fluids are one of the most important groups of industrial lubricants, widely used in industrial hydraulic systems, particularly machine tools, steering gears, etc. Hydraulic fluids are also used in land, sea and airborne transport and in brake systems. Greatly differentiated hydraulic systems, operation in various environmental atmospheres and often at extreme temperatures require a multitude of products of consistently varied properties. As for gear or engine oils, this has led to the classification of hydraulic lubricants, ISO 6743-4:1999, Table 8.5, according to type. It clearly reflects the chemistry of these lubricants, from straight mineral oils, additive treated products that include all the most important additives, emulsions and water-based fluids, to synthetic oils. The classification also takes account of some important properties of these lubricants. Apart from the properties typical for all fluid lubricants, such as viscosity, viscosity index, oxidation resistance, tribological and anti-corrosion properties, the other important features of hydraulic fluids are as follows:

- compressibility, to transmit power successfully a hydraulic fluid must be virtually incompressible
- compatibility with seals, air-release and anti-foam properties, to avoid gas entrapment and increased compressibility
- filterability
- as with engine and gear oils, shear stability in the case of non-Newtonian fluids

Filterability of hydraulic fluids is associated with their purity, an extremely important requirement. High-quality hydraulic fluid must be absolutely free from

Table 8.5 ISO 6743-4:1999 Hydraulic fluid classification for hydrostatic systems

Fluid symbol	General fluid characteristics
HH	Non-inhibited refined mineral oil
HL	Rust and oxidation inhibited refined mineral oil
HM	HL type with improved anti-wear properties
HR	HL type with improved viscosity index
HV	HM type with improved viscosity index
HG	HM type with antistick-slip properties
HETG	Triglycerides (vegetable oils)
HEPG	Polyglycols
HEES	Synthetic esters
HEPR	Poly-alpha-olefins and similar hydrocarbons
HS	Synthetic fluids with no specific fire-resistant properties
HFAE	Fire-resistant oil-in-water emulsions containing maximum 20% mass of combustible materials
HFAS	Fire-resistant solutions of chemical in water containing minimum 80% mass of water
HFB	Fire-resistant water-in-oil emulsions
HFC	Fire-resistant water polymer solutions containing minimum 35% mass water
HFDR	Fire-resistant synthetic fluids based on phosphoric acid esters
HFDU	Fire-resistant synthetic fluids of other types

impurities, especially those causing wear. Some hydraulic fluids, such as HR, HV and HG, have high viscosity indices up to 150 and are required when temperature changes occur within the working range of hydraulic systems.

The selection of hydraulic lubricants and their required properties depend on the operating conditions of the hydraulic system. For systems with a high leakage rate, non-toxic hydraulic lubricants with adequate levels of biodegradability must be used to avoid polluting the environment, the HETG, HEPG, HEES, HEPR classifications. Hydraulic lubricants designed for the food and pharmaceutical industries require products that comply with the foodstuff regulations.

In terms of their chemistry, hydraulic lubricants are divided into four classes: (i) mineral oil-based products, (ii) synthetic lubricants, (iii) emulsions, and (iv) water-based fluids. Biodegradable hydraulic fluids are a new ISO classification group and will be described separately.

8.4.2 Mineral Oil-Based Hydraulic Lubricants

The HH, HL, HM, HR, HV and HG hydraulic lubricants are the most important and widely used. As viscosity is one of their most important properties, they are produced in a wide range of viscosities, ISO VG 10-100. For a given application, viscosity should be as low as possible to give a rapid response for the hydraulic system, meaning that the oil should be sufficiently fluid for efficient power transmission. A minimum viscosity level is necessary to eliminate or minimize leakage losses and ensure lubrication of all tribological elements of the hydraulic system.

Mineral oil-based hydraulic lubricants use mainly paraffinic basestocks to give adequate viscosity/temperature characteristics and are a series of gradually enhanced formulations:

- the HH group are straight mineral oil products
- the HL group have improved performance characteristics and incorporate oxidation and rust inhibitors in addition to the HH group
- the HM group have anti-wear additives in addition to the HL group
- the HV group are lubricants of the HM type containing viscosity index improvers
- the HR group contain oxidation and rust inhibitors plus viscosity index improvers
- the HG group lubricants are formulated with both the above together with anti-stick/slip additives, i.e. friction-modifying additives. Special oils may also contain anti-foam and demulsifying additives

Hydraulic lubricants with particularly low pour points are formulated using naphthenic base oils which have poorer viscosity–temperature characteristics. But at higher pressures naphthenic oils have a significantly greater viscosity increase than paraffinic base oils. In consequence, these oils compensate or even exceed viscosity losses due to heating.

8.4.3 Synthetic Hydraulic Lubricants

Several classes of synthetic oils, such as phosphoric acid esters, polyglycols and silicones, are used as hydraulic lubricants. They are mostly used as fire-resistant lubricants, of importance for coal mines, steel mills and foundries, especially when hydraulic systems operate close to hot areas, e.g. furnaces. Polychlorinated biphenyls, PCBs, are the most fire resistant but are no longer used because of their high and persistent toxicity. Silicones have very poor lubricity and are very expensive, whereas polyglycols with high flash points do not fully meet more stringent fire-resistant requirements. At present, therefore, synthetic hydraulic lubricants are almost exclusively based on trialkyl or triaryl phosphates, or their mixtures, available with a wide range of viscosities and adequate low-temperature properties required for hydraulic lubricants.

The phosphoric acid triesters possess excellent anti-wear properties, see Chapters 3 and 6, and sufficient oxidative stability. Their disadvantage is their ability to hydrolyse, which depends significantly on the structure of the ester; short chain alkyl esters and aryl esters hydrolyse more rapidly than the long-chain alkyl esters. The triaryl versions of phosphate esters are relatively unique among hydraulic fluids because of their self-extinguishing properties, the fluid does not create enough energy to support its own combustion in a fire [65].

8.4.4 Emulsions and Water-Based Fluids

Emulsions are in the HFAE and HFB groups of hydraulic fluids. The HFAE oil-in-water emulsions are more important, having a high water content, with very low flammability and are widely used due to their low cost. However, oil-in-water lubricants have a reduced wear protection compared with pure oils and, in addition, rust/corrosion and bacterial attack give problems. Improvement in these properties is achieved by using rust/corrosion inhibitors, bactericides and, if necessary, anti-wear additives. Suitable emulsifiers ensure good stability of the emulsions.

The HFB group, water-in-oil emulsions, give better lubricating properties and corrosion protection and also generally require less bactericides and rust/corrosion inhibitors.

Water-based fluids containing polymer-thickened aqueous solutions, the HFC group, have superior wear behaviour to the oil-in-water emulsions. These fluids are mixtures of glycol, water-soluble polyethers and polyglycols with rust/corrosion and oxidation inhibitors. To be accepted as a fire-resistant fluid, the water content must be at least 35%. Special polyethers with molecular weights of between 20,000 and 40,000 can be used as shear-stable thickeners for water-based hydraulic fluids. Examples of such thickeners are pentaerythritol-, trimethylolpropane- or glycerol-initiated ethylene oxide–propylene oxide polyethers. The chemistry of synthetic thickeners for water-based hydraulic fluids, their thickening effect and shear stability together with their technical properties have been described in detail [66].

8.4.5 Biodegradable Hydraulic Fluids

Hydraulic oils are used in large quantities in a large variety of applications. They are always susceptible to spillage and pose an immediate threat to the surrounding environment. The industry has developed environmentally acceptable products that retain the major performance properties of mineral oil-based hydraulic fluids. These fluids are the HETG, HEPG, HEES and HEPR groups of hydraulic fluids. The classification requirement for a fluid to be biodegradable is that more than 60% must break down into innocuous products when exposed to the atmosphere over a 28-day period.

Additives produced for mineral oils are not necessarily biodegradable, may be toxic and can inhibit the biological degradation of the base oil. Highly biodegradable additives have been developed for biodegradable hydraulic fluids such as sulphurized fatty materials of animal or vegetable origin for extreme pressure/anti-wear additives and succinic acid derivatives to produce ashless additives for corrosion protection.

Hydraulic fluids based on vegetable oil can be most effective from an environmental perspective. They are a good match for mineral oil-based products on performance and cost-effectiveness. The most popular vegetable oil-based hydraulic fluids contain rapeseed or canola oils, because these have extremely favourable lubricating and anti-corrosion protection characteristics and their viscosity changes only slightly with temperature.

Polyglycols were the first basestocks to be formulated into biodegradable fluids and they are still used widely as fire-resistant lubricants and also in food processing. However, polyglycols lack the required biodegradability performance and are potentially toxic in water when mixed with lubricating additives.

Synthetic ester-based hydraulic fluids are used where application of vegetable oil-based products is limited due to their lower chemical stability; however, their high cost has limited their use. The most commonly used synthetic esters are polyol esters, such as those based on trimethylolpropane and pentaerithritol.

Poly-alpha-olefins and similar hydrocarbons have relatively low volatilities up to 160°C in comparison with corresponding mineral oils and have complete miscibility with esters and mineral oils. Their drawbacks are relatively poor solvency for many additive types and a tendency for low viscosity grades to cause shrinking of some rubber seals.

8.5 Industrial Gear Lubricants

8.5.1 General Description

Gears are machine elements that transmit motion by successively engaging teeth. If two gears run together, the one with the larger number of teeth is called the gear and the one with the smaller number of teeth is called the pinion.

Compared with automotive hypoid gears, gears used in industrial equipment usually operate under moderate loading conditions and place lower demands on the load-carrying capacity of the lubricants. Their typical function is to increase or decrease shaft speeds or to change the direction of drive. Spur gears connect parallel shafts. Worm, bevel or crosshead helical gears are used to change the direction of drive. All of these gears perform their function either with or without alteration in speed. Using worm gears achieves large transmission ratios in one stage and in a small space.

The main functions of a gear lubricant are wear prevention and friction reduction through a lubricating film between the gear mating elements. The two major gear types are enclosed gears and open gears. Enclosed gears may be lubricated by splash where the gearbox lubricant level is maintained such that the teeth of the lower wheel just dip into the lubricant. A pumped lubrication system may also be used where the lubricant is sprayed onto the teeth close to the point of engagement and then recirculated. For enclosed gears the lubricant also has to carry away the heat developed during friction. Open gears are lubricated by applying lubricant to the teeth, e.g. by intermittent spray. Selection of industrial gear lubricants is described in AGMA 9005-D94, by the American Gear Manufacturers Association, classifying industrial gear oils into 13 types, Table 8.6.

Table 8.6 Relation between ISO viscosity grade and the AGMA classification system [67]

AGMA lubricant classification				
	R&O[a]	Comp[b]	EP[c]	Synthetic
32	0			0 S
46	1			1 S
68	2		2 EP	2 S
100	3		3 EP	3 S
150	4		4 EP	4 S
220	5		5 EP	5 S
320	6		6 EP	6 S
460	7	7 Comp	7 EP	7 S
680	8	8 Comp	8 EP	8 S
1000	8A	8A Comp	8A EP	
1500	9		9 EP	9 S
2200	10		10 EP	10 S
3600	11		11 EP	11 S
Note 1	12		12 EP	12 S
Note 2	13		13 EP	13 S

Note 1: KV at 40°C 6120–7480 cSt,
Note 2: KV at 100°C 190–220 cSt
[a] Rust and oxidation inhibited, [b] Compounded with 3–10% fatty or synthetic fatty oils, [c] Extreme pressure

8.5.2 Lubricants

For industrial gears where the conditions of tooth engagement are not excessively severe, and the danger of scuffing is small, mineral base oils may be used. The choice of oil viscosity depends on the transmitted power and pinion speed, Fig. 8.7. In general, the lubricant viscosity required decreases as the speed increases, and

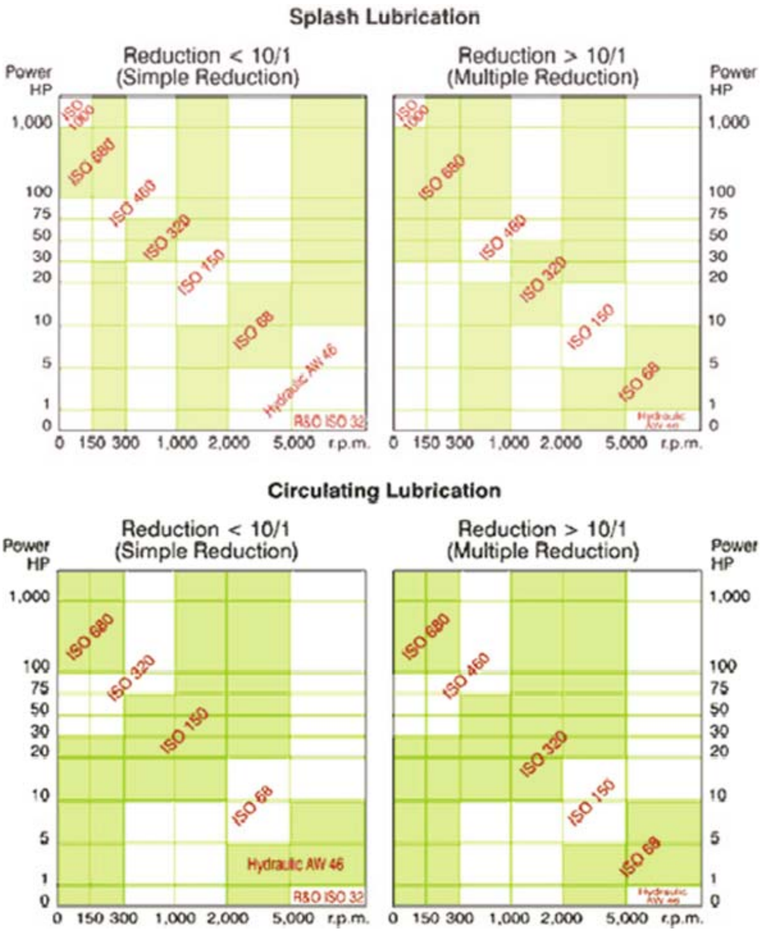


Fig. 8.7 Industrial gear lubricant viscosity selection [68]

increases as the power increases. This applies mostly to low-loaded spur gears, where conditions of the tooth engagement are particularly severe or where gears are subjected to shock loads, the use of tribological additives is essential.

For highly loaded spur, helical, worm and bevel gears, lubricants containing tribological additives such as sulphurized and phosphorus-containing additives are used. These provide excellent anti-wear and extreme pressure protection over a wide range of conditions.

Selecting the proper industrial gear lubricant is important for the long-term life and efficient operation of a gear drive. The four types of industrial gear lubricants that could be used to lubricate industrial gear drives include rust and oxidation (R&O) inhibited oils, extreme pressure (EP) gear oils, compounded gear oils (compounded with 3–10% fatty or synthetic fatty oils) and synthetic gear oils. The relationship between oil ISO viscosity grades and the four types of industrial gear lubricants just described is set out as 13 categories in an extensive table by AGMA 9005-D94 Classification System, the American Gear Manufacturers Association [67], Table 8.6. Table 8.7 presents which type of lubricant is preferred for which type and arrangement of gears.

Table 8.7 Industrial lubricants used with different gears [68]

	Gear type				
	Spur	Helical	Worm	Bevel	Hypoid
Rust and oxidation inhibited	Normal loads	Normal loads	Light loads and slow speeds only	Normal loads	Not recommended
EP gear lube	Heavy or shock loading	Heavy or shock loading	Satisfactory for use in most applications	Heavy or shock loading	Required or specified for most applications
Compounded	Not normally used	Not normally used	Preferred for use by most OEMs	Not normally used	For lightly loaded applications
Synthetic shock loading	Heavy or shock loading	Heavy or use by most OEMs, especially at operating temperatures exceeding 82°C	Preferred for shock loading	Heavy or must contain extreme pressure additives	Gear lubricant

High-viscosity residual lubricants with good adhesion are used for open gears, such as asphaltic lubricants. Special greases and semi-fluid gear lubricants are also used, for example, a lithium soap/synthetic oil-based lubricant provides outstanding low steel/bronze frictional characteristics over wide temperature ranges and long life properties. Industrial gear lubricants for more severe conditions are based on synthetic lubricants such as polypropylene glycol, their characteristics being high load-carrying capacity, very high viscosity index and low pour point, also possessing low frictional characteristics which give more power transmission. Synthetic gear oils generally comprise oils based on synthetic hydrocarbon oils, polyglycols and esters.

Polyglycols have especially low friction coefficients and together with the appropriate additives, they provide excellent anti-wear protection in steel/bronze worm gears and have a good extreme pressure performance [69]. For gear systems, higher polarity polyglycols have greater interaction on the metal gear surface, giving polyglycols mild extreme pressure performance even without additives. Polyglycol oils may have a negative impact on sealing materials and may dissolve some paints; at operating temperatures above 100°C only seals made of fluorinated rubber or PTFE are resistant. Before using these oils in production applications, compatibility tests with paints, seals and sight glass materials are advisable. Since predominantly water-soluble polyglycols are used in gear construction, the influence of water on polyglycols has been examined [70]. Results show that the oils tested were still able to meet CLP requirements, according to DIN 51517 standard, even with a high water content.

Polyglycols are neutral towards ferrous metals and almost all nonferrous metals but if the application has a loaded contact with one component consisting of aluminium or aluminium alloys, such as rolling bearing cages containing aluminium, there may be increased wear under dynamic load such as sliding movement and high load. For such cases, compatibility tests should be conducted. For an aluminium bronze alloy worm gear, polyglycols should not be used because reaction in the load zone may give increased wear [69].

Ester oils have a high thermal resistance and excellent low-temperature behaviour [69]. Rapidly biodegradable ester oils will gain importance in industrial applications because it is possible to achieve the same efficiency as for polyglycol oils by selecting an appropriate ester base oil. However, certain ester oils may exhibit low hydrolytic stability.

8.6 Turbine Lubricants

8.6.1 General Description

There are three main categories of turbines: (i) gas turbines, (ii) steam turbines and (iii) water turbines. Gas turbines are mostly used in aircraft (Chapter 11), though aircraft-derived gas turbines are used for naval vessel propulsion, for stand-by generation of electricity and gas pipeline compression. Steam turbines have become increasingly compact in design and run under more vigorous conditions.

8.6.2 Industrial Turbine Lubricants

No moving parts are involved in the combustion process of gas turbines; therefore, the turbines make little demand on the lubricant and present few lubrication problems. Gas turbines for industrial applications have evolved from steam turbine practice, thus they are similar in design and lubrication requirements except that operating temperatures are much higher. Accordingly, steam turbine lubricants can often be used in industrial gas turbine lubrication but for particularly high temperatures, synthetic lubricants are required.

In steam turbine lubrication systems, a pump transports lubricant from the storage tank through a filter and oil cooler to all lubrication points. Consequently, the lubricant must give reliable lubrication and also serve as a coolant, hydraulic fluid, gear lubricant for geared turbines and also prevent rusting of the turbine components. As the oil is in intimate contact with steam, condensation water, metals and air, it needs high oxidative stability and satisfactory separation from water. To prevent malfunction of the turbine hydraulic system, such as the governors and other control gears, a low air entrainment is essential. These requirements are met by special turbine lubricants, usually formulated with highly refined paraffinic base oils of high viscosity–temperature characteristics and adequate oxidation and corrosion inhibitors. These oils have excellent oxidation stability, very high demulsibility and resistance to foaming and also rapidly release entrained air. ISO VG 32 and 46 oils are usually used for turbines without transmissions; ISO VG 68 is applied only for integral gear lubrication due to its higher viscosity and increased lubrication properties. However, lower viscosity oils such as ISO VG 46 with improved wear protection require less energy to circulate and ensure better heat removal from bearings.

Formulating steam turbine oils is a delicate balance of the correct additives and base oils. Most turbine oils are now formulated with API Group II base oils and contain less than 2% additives [71]. Addition of oil-soluble foreign materials to the product can upset the balance of the formulation and adversely affect product performance. Figure 8.8 shows a typical steam turbine oil composition.

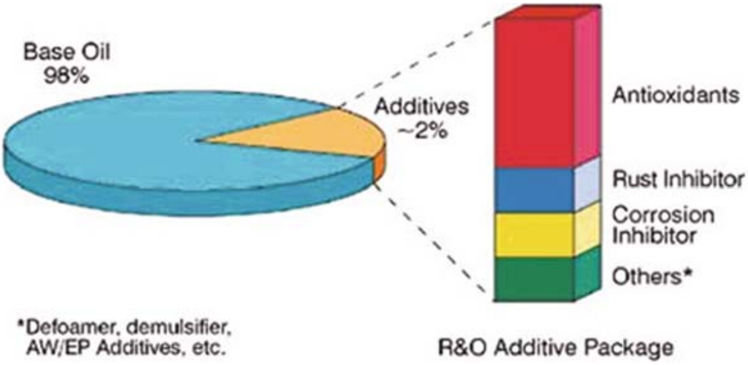


Fig. 8.8 Typical steam turbine oil composition [6]

High-quality steam turbine lubricants usually satisfy the demanding requirements of modern, high-output steam turbines, including their geared units, and are also used for industrial gas turbines and water turbines. In addition to turbine oils being used for electric power plant turbines they are also used for turbo-machinery like turbine compressors of chemical plants. Additionally, turbine oils can be used for hydraulic systems as hydraulic oils in these systems.

The design of steam turbine lubricating oil systems has been established for many years. Steam turbine lubricating oils have two functions, one for lubrication of the turbine bearing and the other to stop steam leakage through the labyrinth seals. The oil tanks are relatively large, turbine temperatures are not very high and oil flow rates are not too high. There is no specific problem concerning oil ageing except water ingress to the steam turbine oils.

It is of particular interest that modern gas turbine oils suffer from varnish formation which in some way relates to highly refined base oils containing low aromatic compounds and low sulphur compounds. Although an incidental relationship between varnish formation and the base oils is not yet clarified, it is worthwhile mentioning that some aromatic compounds and sulphur compounds would retard oil oxidation [72].

Investigation of the final, ‘last chance’, filter of the hydraulic circuit and the main online filter of the lubricating oil revealed that static electricity spark discharges, which happen in the online filter in the lubricating oil, damage the oil and that the outside surface of the ‘last chance filter’ removed the contaminants produced in the lubricating oil line [73]. Clear evidence of spark discharges of static electricity was found on the lubricating oil filter elements and the details of the filter elements investigation and one of the root causes of varnish formation in gas turbine oil systems discussed [74]. It was verified that filtration generates static electricity and that the oil filtered for 30 days at room temperature oxidized faster than the heated oil at 80°C for 6 months.

Earlier work described static electricity generation during filtration and the oil auto-oxidation due to spark discharges, respectively [74, 75]. It was considered that there are overlooked factors like ‘hot spots’ which produce varnish in gas turbine systems. Thus, spark discharges of static electricity have a strong influence on oil oxidation. A new, simple method to test formation of varnish has been proposed [76]. Typical varnish problems are shown in Figs. 8.9 and 8.10.

Fig. 8.9 Varnish on gas turbine valve piston [76]

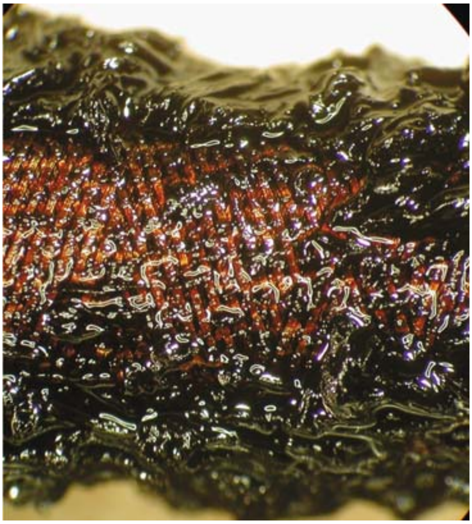


Fig. 8.10 Varnish causes plugging of a pencil filter [76]

8.7 Metalworking Lubricants

8.7.1 General Description of Metalworking Processes

The purpose of metalworking processes is to create a new shape where usually two solids are in contact, the tool and the workpiece. The contact involves either plastic flow of metals, which are metal forming processes, or creation of a new shape by the controlled removal of excess material, which are metal cutting processes. Creation of new shapes by metalworking processes involves high friction, high temperatures and tool wear. Consequently, metalworking lubricants influence both the effectiveness of these processes and the overall efficiency of manufacturing operations [77].

Plastic deformation processes change shape by deforming the workpiece without fracture due to its ductility, distinguishing steady-state and non-steady-state processes [78], a distinction highly significant in terms of lubrication. In steady-state processes such as rolling, the surface of the workpiece arriving at the deformation zone should be lubricated with a fresh lubricant film. For non-steady-state processes the pre-applied film must suffice in the course of deformation and re-application is not usually feasible unless the process is interrupted. Some processes have a transitory character, for example, deformation is non-steady-state at the beginning and end of extrusion but has steady-state characteristics during the greater part of long billet extrusion.

When the new shape is obtained by removing material in the form of chips, the operation is referred to as metal cutting, Fig. 8.11, which shows two important processes: (i) formation of a chip from the workpiece by the tool and (ii) movement of the chip across the face of the tool. Thus it is extremely important to supply a lubricant which reduces friction and removes heat as rapidly as possible, Fig. 8.11, which also shows that the area of highest temperature generated during cutting is at the tool tip. The heat generated is related to frictional heat and the heat generated during the deformation of the metal.

In less severe metalworking operations, hydrodynamic lubrication predominates. In this case, the film thickness at the tool–workpiece interface is sufficient to avoid

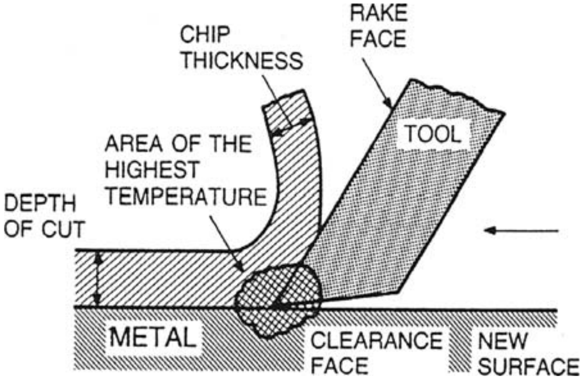


Fig. 8.11 Basic cutting action and chip formation, redrawn and adapted from [77]

contact between the solid surfaces. The film thickness is very large compared with the average size of lubricant molecules, Fig. 8.2, so that the physical and macroscopic properties, especially viscosity, are significant. Severe conditions of deformation constitute the boundary lubrication regime wherein the chemical and physicochemical properties of the lubricant, particularly the additive system contained within the lubricant, become of great significance. The thickness of the boundary film is greatly reduced and, in some cases, such as iron chloride, can be of the same order of magnitude as the lubricant component molecules, Fig. 8.2.

An effective film interposed between the tool and the workpiece prevents welding of the surfaces. In the case of load-carrying additives, such as organosulphur compounds and chlorinated hydrocarbons, the primary film formation takes place by direct chemical reaction between the additives and the surfaces. This type of chemical reaction causes a kind of chemical wear which, however, is not related to material loss due to straight chemical attack but is rather the material loss due to tribochemical reactions. The tribochemical process consists of the following stages [77]:

(i) a film is formed on the surface of the die and/or workpiece through tribochemical reaction, e.g. extreme pressure additives or soap-film formation on reactive surfaces,
(ii) the reaction product is mechanically removed in the deformation zone and enters the bulk lubricant or is deposited on the workpiece,
(iii) the highly reactive surface thus produced is recoated with the reaction product if the reactivity of the lubricant or environment is adequate. As for all chemical reactions, this too is greatly accelerated by temperature and pressure.

It is usually preferred that the workpiece should wear, although in the case of non-reactive materials die life may have to be sacrificed if complete separation of die and workpiece cannot be achieved. Tribochemical wear, to some extent, is sacrificial wear; protection from the more severe forms of adhesive wear is achieved at the expense of some high material loss through tribochemical action.

Tool wear in metal forming is affected by many factors, such as tool pressure, the sliding speed and the enlargement of the surface. Test methods are available to investigate the effects of these factors. It is impossible, however, to draw from the test results a general understanding of the effects of these factors on tool wear, because in the test methods some of the factors could not be well controlled [79]. New test methods for tool materials were proposed for metal forming which can be carried out with apparatus which is widely used, such as a lathe, a dynamometer and a surface roughness meter [79].

An analytical method was developed which enables the crater and flank wear of tungsten carbide tools to be predicted for a wide variety of tool shapes and cutting conditions in practical turning based only on rectangular cutting data machining and two wear characteristic constants. An energy method was also developed to predict chip formation and cutting forces in turning with a single-point tool from the rectangular cutting data. Stress and temperature on the wear faces can be calculated based on these predicted results [80].

Wear rates of several commercial ceramic cutting tools were measured when machining an austempered ductile iron. As cutting speed increased, the flank wear rate per cutting distance increased slightly for alumina inserts containing titanium carbide but, by contrast, is decreased for zirconia-toughened alumina inserts. The difference was explained for the zirconia-toughened alumina ceramic as the monoclinic-to-tetragonal transformation of zirconia being an important wear mechanism in controlling tool life due to elevated cutting temperatures [81].

8.7.2 Lubricant Types for Metal Forming Processes

Metal forming processes encompass rolling, extrusion, drawing such as drawing tubes, tube bending, deep drawing, wire forming, forging, hydroforming and sheet metal forming. The operations are performed under both ambient and high temperatures, referred to as either cold-working or hot-working processes. The hot-working processes generally include bulk deformation processes, known as primary metalworking processing. Secondary metalworking processes involve cold operations, such as rolling, drawing and extrusion.

The lubricant used in a given metal forming process should primarily reduce friction which generally affects tool life, metal flow, energy consumption, heat evolution and surface finish. Usually the lower the friction coefficient, the higher the reduction in forces and power required. For example, good lubrication in forging reduces die wear and forging load, prevents die seizure and helps release the forged part from the dies. Furthermore, it improves material flow in the dies and acts as a thermal barrier between the workpiece and the die surfaces. However, in rolling, the coefficient of friction between the work rolls and the rolling stock should be neither too high nor too low. Clearly, low friction reduces energy consumption, heat evolution and roll wear but if the friction is too low then slipping may occur which may damage the surface of the rolling stock and has a negative effect on the forming process.

Liquid lubricants, suspensions, pastes, greases, solid lubricants and coatings are the lubricants of choice for metal forming processes. Since the metal to be formed may vary widely in composition, from almost pure metals such as aluminium, beryllium, copper, magnesium, nickel, titanium, to very complex alloys such as stainless steels, a wide variety of liquid, semisolid and solid lubricants, as well as their combinations, can be used for special forming operations. The lubricants most commonly used include mineral oils, mineral oils plus fatty oils (compounded oils), emulsions (soluble oils and semisynthetic/synthetic fluids), synthetic oils, graphite suspensions, esters, fatty acids, fatty compounds, lanolin, tallow, paraffin waxes, polymers, conversion coatings (involving the reaction of the surface of the workpiece material with selected anions), copper plating for refractory metals, graphite, molybdenum disulphide, salts, glass, soaps, aqueous solutions, bentonite, lime, mica, talc and others.

Additives used for metal forming lubricants primarily include extreme pressure agents such as sulphurized fats and oils, sulphochlorinated fats and oils, anti-weld agents, corrosion inhibitors, buffers (alkaline reserve), biocides and chemicals used to formulate emulsions. Fatty acids or fatty compounds, as well as graphite or molybdenum disulphide, can also be used as additives.

Different metal forming processes require different lubricants, for example, during compression of a workpiece between dies or platens such as in forging, coining and up-setting processes, any impact splashes out the liquid lubricant. Hence a solid lubricant is more effective, such as PTFE [82].

Lubricants for metal forming play a critical role in many manufacturing processes and contribute to the success or failure of the process, productivity, worker safety, energy consumption and environmental impact. The complex problems of lubricating metal forming processes may be illustrated by the aluminium rolling process, which includes both hot and cold rollings. Generally aluminium or aluminium alloy sheets are made by hot rolling of large ingots to a thickness of about 3–17 mm, which are then reduced further by cold rolling.

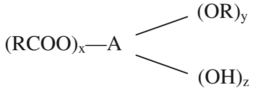
Oil-in-water emulsions containing approximately 2–5% of an oil concentrate are mostly employed as lubricants and coolants for hot rolling. The concentrate may be composed of 70–80% naphthenic or paraffinic oil, 15–20% of anionic and/or non-ionic emulsifiers and 5–10% other ingredients [7]. The other ingredients may be many compounds of the following additive groups: load-carrying (tribological) additives, oxidation inhibitors, wetting agents, bactericides and defoamers. They may include oleic add and/or other fatty derivatives, phosphoric acid esters (e.g. tricresyl phosphate), ethanolamines and other compounds.

During hot rolling, the most important function of the lubricant is cooling but it should also reduce energy consumption, provide good surface quality of the rolling stock and achieve maximum thickness reduction of the rolled material. Thus, friction is also important.

During cold rolling, hot rolled strips are reduced at ambient temperature to a sheet or foil. Since aluminium tends to transfer to the rolls during cold rolling, as with the hot rolling process, the primary function of lubricants for cold rolling is to reduce this tendency. Highly refined, narrow distillate fractions of paraffinic crude oils are mostly used as base oils for these lubricants. The annealing temperature in the aluminium industry is approximately 320°C, thus it is convenient to use mineral oil fractions with a boiling range not exceeding this temperature. Consequently, these base oils are from kerosene cuts and to provide aluminium cold rolling lubricants with suitable frictional characteristics and load-carrying capacity, a package of special additives must be added to the low-viscosity mineral base oils. The additives used comprise mainly fatty alcohols, fatty acids and fatty esters. Fatty alcohols ensure better performance of the lubricant since they do not affect the annealing properties of aluminium.

The tribochemical reactions of these additives with aluminium are very interesting, especially from the point of view of organometallic products resulting from alcohols. The aluminium rolling process produces abrasive particles and organometallic compounds, mostly called soaps, resulting from the reaction between fatty additives and the fresh unoxidized metal surfaces produced during plastic deformation [83]. Fatty acid soaps are well known and broadly discussed in the literature; however, few papers deal with direct reactions of fatty compounds with aluminium. It has been shown that esters, alcohols and ethers can react with an uncontaminated fresh aluminium surface [84]. It has been suggested that during lubrication, alkoxide formation from alcohols and soap formation from esters can occur. Products have been described resulting from tribochemical reactions between aluminium and foil-rolling kerosenes containing fatty acids and fatty alcohols as additives [84]. Organometallic products were isolated and analysed and it was suggested that during plastic deformation fatty acids react directly with aluminium to yield polymeric soaps. Fatty alcohols can lead to a similar reaction but on a smaller scale. In this case, a part of the alcohol was assumed to be changed into acid which can react to give an ester and a blend of hybrid soaps of the general formula, Fig. 8.12.

Fig. 8.12 Aluminium alkoxides, formed from alcohols and acids



$$(RCOO)_x{-}A \begin{cases} (OR)_y \\ (OH)_z \end{cases}$$

where x = 1, 2 or 3 and x + y + z = 3.

On the other hand, the negative-ion-radical lubrication mechanism of alcohols gives a clear explanation of the formation of aluminium alkoxides, i.e. the $Al(OR)_y$, part of the hybrid soap, from alcohols [85]. The mechanism is based on the low-energy electron, 2–4 eV, emission process from the aluminium surface. The emitted electrons and alcohol molecules produce negative and radical-negative ions, including $R{-}CH_2{-}CH_2{-}O^-$ ions which give alkoxides by reacting with the positively charged sites on the deformed aluminium surface. This model elucidates the formation of aluminium methoxide and aluminium butoxide on aluminium surface prepared by cutting under high vacuum [86], conducted in a special vacuum chamber. A small lathe in the chamber held an aluminium disc mounted on a drive shaft rotated using a magnetic assembly. Reactants were introduced into the chamber through a variable leak valve and the components in the chamber analysed by a mass spectrometer. The rate of chemisorption was proportional to the cutting speed and chemisorption took place not only during cutting but also after cutting. The hydrogen concentration increased during cutting. The reaction mechanism is explained by the Kajdas negative-ion-radical model as follows [85]:

- the cutting process is associated with the electron emission, similar to the emission caused by plastic deformation, which is responsible for the rate of chemisorptions,
- thus, the exoemission process is the main factor governing the reactivity of methanol and butanol towards aluminium,
- it is known that the exoelectron emission rapidly reaches a maximum during rubbing and then, after rubbing, decays with time,
- this explains why chemisorption takes place after cutting,
- hydrogen radical recombination is responsible for the hydrogen formation during cutting.

The above examples demonstrate the complexity of metalworking lubrication and also give evidence that mechanical activity at metalworking surfaces promotes chemical reactions and produces a surface chemistry that may be entirely different from that observed in static studies, i.e. those activated predominantly by temperature. The metalworking process itself initiates and accelerates chemical reactions which would otherwise take place only at much higher temperatures or not at all and such enhanced surface activity might be represented as follows [87]:

$$\text{Enhanced reactivity} = \text{Exoelectron} + \text{Elevated temperature} + \text{High pressure}$$

8.7.3 General Lubricant Types for Metal Cutting Processes

The main functions of a lubricant in a metal cutting process are to lubricate or reduce friction between the tool and the workpiece and to act as a coolant by rapidly removing heat generated at the tool/workpiece interface. There are three major types of metal cutting lubricants: oils, emulsions and water-based products.

Emulsions contain oil, such as mineral or compounded oil, usually in proportions of 3–10%, in the form of suspended droplets dispersed with the aid of emulsifiers. They are used where rapid heat removal is a major requirement. The additives used are usually rust inhibitors and EP additives. Water-based products, also known as water-soluble fluids, chemical fluids or synthetic fluids, do not contain oil, but only water-soluble chemicals. Water-based lubricants comprise, for example [88] the following:

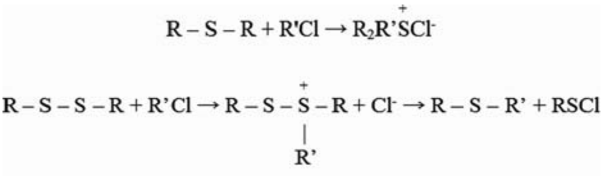
- mixture of salts of alkylaryl sulphonic acids,
- complex phosphate surfactants,
- phosphate esters and sulphur compounds,
- disodium monocupric citrate,
- zinc phosphate,
- sulphurized molybdenum compounds,
- modified triglycerides.

Oil-based lubricants comprise [89], for example, the following:

- chlorinated hydrocarbons,
- organic hydroperoxides and sulphur,
- sulphurized oil and poly-alkenylsuccinic anhydride-polyglycol reaction products,
- partially neutralized aluminium acid alkylorthophosphates.

Such oils are used in tough cutting operations such as tapping, threading and broaching. Lubricity and anti-weld characteristics are important characteristics of these cutting oils. These oils are derived from petroleum, vegetable and animal sources and usually contain various types of additives.

Mixtures of sulphurized and chlorinated additives give a synergistic effect, relating to the well-known fact that molecules containing both chlorine and sulphur or a mixture of sulphur- and chlorine-containing compounds show enhanced film strength formation during metalworking. The effect was explained in terms of the chemical reactivity of the additives used and their ability to release the load-carrying element for reaction with the metal surface as the following reaction sequence [90]:



$$R-S-R+R'Cl \rightarrow R_2R'\overset{+}{S}Cl^-$$

$$R-S-S-R+R'Cl \rightarrow R-S-\underset{\displaystyle R'}{\overset{+}{S}}-R+Cl^- \rightarrow R-S-R'+RSCl$$

$$RSCl+R'Cl \rightarrow R-S-R'+Cl_2$$

(Reaction sequence 8.1)

Organochlorine compounds with monosulphides form simple sulphonium ions, but disulphides offer the possibility of more reactive species which can increase the lubricating properties of the system. Recently, the synergistic behaviour of chlorinated paraffin in dibenzyl disulphide has been explained in terms of the negative ion-radical action mechanism [85, 91]. The reaction of these compounds with electrons of low energy, 1–4 eV, emitted during the friction process, reactions of thermal decomposition and reactions of ions with radicals are presented as the following reaction sequence:

$$\begin{gathered} R_1Cl+e^- \rightarrow R_1^{\bullet}+Cl^- \\ R_1Cl \rightarrow R_1^{\bullet}+Cl^{\bullet} \\ Cl^-+Cl^{\bullet} \rightarrow Cl_2^{\bullet-} \end{gathered}$$

(Reaction sequence 8.2)

Reactions involving radical anions and radicals are summarized as the following reaction sequence:

$$\begin{gathered} RSSR+e^- \rightarrow RS^{\bullet}+RS^- \\ RS^{\bullet}+e^- \rightarrow RS^- \\ RSSR \rightarrow 2RS^{\bullet} \\ RSSR+e^- \rightarrow RSSR^{\bullet-} \\ RS^-+RS^{\bullet} \rightarrow RSSR^{\bullet-} \end{gathered}$$

(Reaction sequence 8.3)

Reactions between radical anions involving different elements are summarized as the following reaction sequence:

$$\begin{aligned} &RS^{\bullet}+Cl^- \Leftrightarrow RSCl^{\bullet-} && \text{(i)} \\ &RS^{\bullet}+Cl_2^{\bullet-} \Leftrightarrow RSCl^{\bullet-}+Cl^{\bullet} && \text{(ii)} \\ &RSCl^{\bullet-}+RS^- \Leftrightarrow RSSR^{\bullet-}+Cl^- && \text{(iii)} \\ &RSCl^{\bullet-}+RS^{\bullet} \Leftrightarrow RSSR+Cl^- && \text{(iv)} \\ &2RSCl^- \Leftrightarrow RSSR+2Cl^- && \text{(v)} \\ &RSSR^{\bullet-}+R_1Cl \Leftrightarrow RSSR+R_1^{\bullet}+Cl^- && \text{(vi)} \end{aligned}$$

(Reaction sequence 8.4)

Reaction (8.5)(iv) results in the formation of the less reactive disulphide from the more reactive thiyl, $RS\cdot$, radical and thiolate anion, $RSCl^{\bullet -}$. This explains the smaller amount of sulphur product formation in boundary lubrication with dibenzyl disulphide and chlorinated paraffin [91]. Assuming this to be the case, electron transfer between an initially formed disulphide radical anion and a chlorinated paraffin appears to be an additional explanation for the increased reactivity of chlorinated paraffin in the presence of disulphide.

Recent concerns about environmental issues have highlighted problems with using lubricants containing chlorinated chemical compounds. An approach to improving metalworking lubricants was proposed by using micellar copper oxide as a multifunctional anti-wear and friction-reducing additive [92]. The soft-core reverse micelles, RMs, formed in oil-based fluids and hard-core RMs in water-based fluids are most important in transferring additives during tribochemical processes, Fig. 8.13:

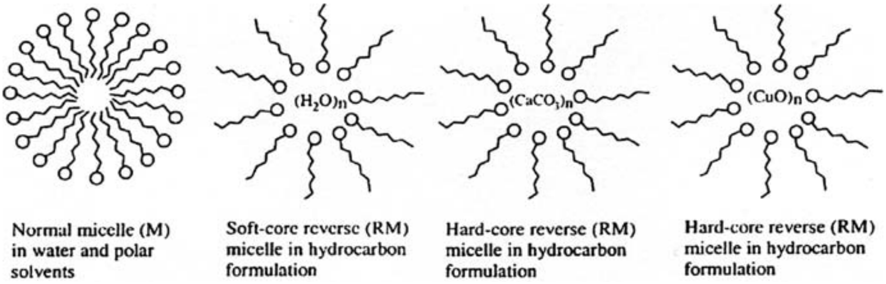


Fig. 8.13 Schematic representation of normal micelle (M) in water, soft-core reverse micelle (RM) and hard-core reverse micelle (RM) in hydrocarbon formulation; /\/\/\/O, detergent molecule [92]

The formation of a copper tribofilm takes place during the friction process and disintegration of the RMs takes place in a tribochemical reaction as follows:

$$Cu^{2+} + 2e^{-}_{tribo} \rightarrow Cu^{0} \qquad \text{(Reaction 8.5)}$$

creating copper tribofilms at the contact of the tool and the workpiece which can reduce cutting forces and the wear of cutting tools.

NIOSH, the (US) National Institute for Occupational Safety and Health, reported that fluid complexity in use is compounded by contamination with substances from the manufacturing process, such as tramp oils, hydraulic fluids and particulate matter from grinding and machining operations. Furthermore, water-based metalworking fluids support microbial growth which introduces biological contaminants such as bacterial and fungal cells or cell components and their related biological byproducts such as endotoxins, exotoxins and mycotoxins. Therefore, worker exposure to metalworking fluid mist has been of concern to the metalworking fluid industry recently [93]. Fluid mist is formed through three basic mechanisms: (i) the formation of vapour, (ii) mechanical action of machining and (iii) the volatile nature of components within the metalworking fluid. To reduce and solve this problem, anti-mist additives have been developed, mainly polymers that stabilize the metalworking fluid against break-up during machining [94]. Most anti-mist polymers are either polyisobutylene, polyethylene oxide or associative polymers. The first polymer can be used in straight oil systems while the latter two are suitable for water-dilutable fluids.

It is well known that forming stable oil-in-water metalworking emulsions involves significant amounts of emulsifiers (detergents) and considerable energy of mixing. In addition to the costs of using detergents, there is an environmental cost during disposal and the problem of leaving residues on surfaces. It has recently been found that removing the gases dissolved in oil and water allows them to form a stable emulsion [95]. No emulsifying additives are required and the emulsions form with only minimal shaking; however, an efficient and affordable technology of degassing has still to be developed.

Although many alterations have been made to the formulation of metal cutting lubricants since their introduction, the basic functions have remained unchanged as (i) cooling of the workpiece and chips to improve tool life and permit higher cutting speeds, as well as to reduce distortion and maintain dimensional accuracy; (ii) lubrication to reduce friction, improve surface finish of the metal cut, protect the newly machined surfaces from rust/corrosion and buildup of undesirable deposits, and to reduce both tool wear and the tendency for vibration and chatter; (iii) safety in use for the operators and (iv) flushing the chips produced from the cutting zone.

The hardness of the metal is an important property. As hardness increases, so does tool wear and thus the lubricating properties of cutting fluids become significant. Almost as important as the type of metal is the severity of the machining operation in cutting fluid selection, Fig. 8.14. Turning is the least severe operation where heat is easily removed by the cutting fluid and the unconfined flow of the chip. Internal broaching is the most severe operation where each cutting tool is in contact with the workpiece during the entire cut and, with each succeeding cut, the tool is buried deeper into the workpiece. This makes it difficult for the cutting fluid to reach the tool tip during machining. Consequently, cutting fluids used in

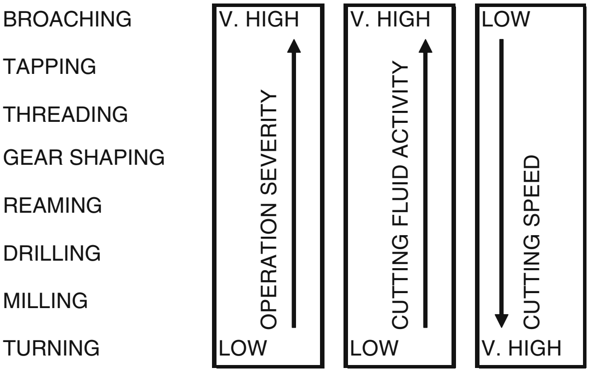


Fig. 8.14 Relative severity of some metal cutting processes, redrawn and adapted from [97]

broaching must have very good anti-weld and lubricating properties to protect the cutting tool and ensure proper finish and accuracy. Figure 8.14 shows that increasing operational severity is usually accompanied by decreasing cutting speed. More severe operations demand more active cutting fluids, which means that cutting fluids with additives, particularly of the extreme pressure type, must be used under severe operational conditions. Modern cutting fluids contain a wide variety of speciality chemicals designed to supply a definite degree of lubricity, surface activity, stability and anti-weld properties [96].

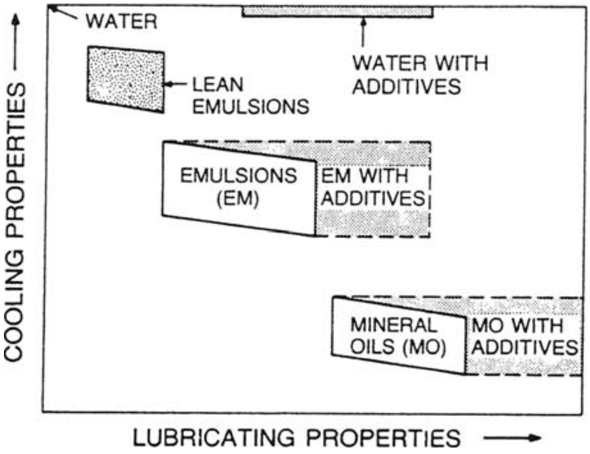


Fig. 8.15 Lubricating and cooling properties of metalworking liquids

The influence of operational severity on the cutting fluid requirements may be summarized as follows:

(i) High cutting speeds normally generate higher temperatures. In these cases, low cutting fluid activity is required, but cooling of the cutting area becomes crucial and thus metal cutting lubricants that possess great cooling power are of importance. Water is one of the best coolants known but is a very poor lubricant. Consequently, water-based products containing wetting agents, extreme pressure additives, corrosion inhibitors and other chemicals are the frequent choice of metal cutting fluids for turning, milling, drilling and other processes of low operational severity. Figure 8.15 shows that some metal cutting fluids have excellent cooling properties and may also provide good lubricating properties.

(ii) In lower speed processes that involve high tool wear and friction, such as gear cutting, tapping or broaching, lubrication is critical and cooling is of lesser importance. In such cases, associated with very high operational severity, oil-based lubricants with additives, mainly of the extreme pressure type, are most frequently used. The chemistry of additives used in metalworking lubricants has been described in detail [98].

Finally, an interesting trend in metal cutting lubrication has developed due to adverse effects of the use of cutting fluids and environmental concerns with regard to cutting fluid disposability. Industry is increasingly compelled to consider 'dry machining' or 'near-dry machining', with the aim of eliminating or significantly reducing the use of metalworking fluids [99]. Pending EPA regulations on metal cutting, dry machining is becoming an important topic of research and investigation, in both industry and government research laboratories. Although the need for dry machining may be apparent, most of the manufacturers still consider dry machining to be impractical and even if possible, very expensive. This perception is mainly due to a lack of appropriate cutting tools that can withstand intense heat and 'built-up-edge', BUE, formation during dry machining. The challenge of heat dissipation without coolant requires a completely different approach to tooling. Special tooling utilizing high-performance multi-layer, multi-component, heat-resisting, low-friction coatings could be a plausible answer to the challenge of dry machining. As such coatings, the following materials are considered: nanocrystalline near frictionless carbon, NFC, diamond-like coatings, DLC, composite coatings such as titanium aluminium nitride, TiAlN, tungsten carbide/carbon, WC/C and others or multi-layer multicomponent nanocoatings such as TiAlCrYN and TiAlN/YN.

8.8 Speciality Lubricants

8.8.1 Process Oils

Process oils are not typical lubricants and are mostly used as processing aids in manufacture. They are generally additive-free mixtures of crude oil hydrocarbons and include products such as (i) medicinal white oils, (ii) technical white oils, (iii) bright process oils and (iv) dark process oils. Medicinal white oils are composed exclusively of isoparaffins and alkylnaphthenes. Technical white oils are less refined products than medicinal white oils and are composed of saturated hydrocarbons, though they may also contain a slight amount of aromatic compounds. Bright process oils include both yellow raffinates and brown distillates. Dark process oils are extracts from solvent refining of mineral base oils.

Process oils are widely used in various industrial processes, including rubber, plastics, pharmaceutical, food, cosmetics, printing ink, textile and other industries.

8.8.2 Textile Oils

These oils are used in the fibre and textile industries either to lubricate the textile machinery or as components of process oils used for the working of natural fibres, the production and processing of synthetic fibres or the finishing of intermediate or final products. Textile oils are often made from technical white oils and oxidation inhibitors plus agents ensuring removal of the oils by washing, even after a long period of use. High-quality products also contain additives that assist in removing oil stains from the fabrics.

8.8.3 Food-Grade Lubricants

Food-grade lubricants find application in the food and pharmaceutical industry. Such lubricants must resist degradation from food products, chemicals and water/steam, must have a neutral behaviour towards plastics and elastomers and have the ability to dissolve sugars. These oils must also comply with food/health and safety regulations, as well as be physiologically inert, tasteless, odourless and internationally approved [100].

Food-grade lubricants are based on white mineral oils, synthetic oils such as polyalphaolefins and polyalkylene glycols, or vegetable oils. Additives for food-grade lubricants should also fulfil safety requirements, for example, as anti-wear and friction-reducing additives for white mineral oils, 'CHO', i.e. only consisting of carbon, hydrogen and oxygen compounds, mostly ester-type products, have been proposed [4].

The United States Department of Agriculture, USDA, created the original food-grade designations H1, H2 and H3. H1 lubricants are food-grade lubricants used in food-processing environments where there is the possibility of incidental food contact. H2 lubricants are non-food-grade lubricants used on equipment and machine parts in locations where there is no possibility of contact. H3 lubricants are food-grade lubricants, typically edible oils, used to prevent rust on hooks, trolleys and similar equipment. The German Institute for Standardization (DIN) submitted German standard DIN V 0010517, 2000–08, as a draft to the International Organization for Standardization, ISO, in Geneva. It may take a few years from the application date for it to be accepted for an international standard to be released.

8.8.4 Slideway Oils

Slow moving slides and tables in machine tools are subject to jerky motion due to alternating slipping and sticking of the sliding surfaces. Consequently, specially developed lubricants are required to prevent and/or reduce the stick-slip phenomenon. Slideway oils usually contain polar surface-active compounds, mostly fatty acid derivatives, together with anti-wear additives and oxidation inhibitors. The polar surface-active agents form oriented boundary layers which prevent adhesive friction.

8.8.5 Cylinder Oils

These products are highly viscous mineral oils produced from raffinates of high boiling vacuum residues or from brightstocks and fatty oils. The latter improve water displacement characteristics of the cylinder oil and provide better adhesion of the lubricating film to the cylinder walls. Cylinder oils, also known as compounded cylinder oils, are used for lubricating cylinders, valves and other moving parts of steam engines.

8.8.6 Wire Rope Lubricants

Wire rope lubricants have two principal functions, to reduce friction as the individual wires move over each other and to provide corrosion protection and lubrication for the core and inside wires and on the exterior surfaces [101]. There are two types of wire rope lubricants, penetrating and coating. Penetrating lubricants contain a petroleum solvent that carries the lubricant into the core of the wire rope then evaporates, leaving behind a heavy lubricating film to protect and lubricate each strand. Coating lubricants penetrate slightly, sealing the outside of the cable from moisture and reducing wear and fretting corrosion from contact with external bodies. Wire rope lubricants include straight mineral oils, bituminous materials, adhesive compounds, vegetable oils and water displacement agents. A wide variety of product types are used depending upon the severity of service conditions. Where wire ropes are used in exposed locations, the lubricant should be resistant to weathering.

8.8.7 Other Lubricants and Related Products

Coupling fluids are low-viscosity lubricants with high oxidative stability. Low-viscosity gear oils and engine oils may also be used for simple transmissions.

Chains used in industry are lubricated with heavy oil or grease and should have sufficiently low viscosity and ability to maintain lubricating qualities under different temperatures, moisture, etc. [102]. In extremely dusty environments a solvent containing anti-wear additives is used. If the chain is running through and/or is immersed in water, a combination of penetrating oil and tacky grease is the best method.

Lubricating oils for precision instruments and large clocks must have excellent oxidation stability, good anti-wear and anti-corrosion properties and retain their viscosity over a long period of time. Sometimes small amounts of gel-forming soaps, e.g. an aluminium soap, are added in order to reduce the creeping effect.

Efforts have also been made to cover several applications with one oil. Thus, some multipurpose lubricants have been proposed, e.g. combinations of hydraulic lubricant, metalworking fluid and gear lubricant. Usually, multipurpose lubricants require relatively high levels of additive treatment.

Finally, there are oils whose function is not related to lubrication, such as heat transfer oils, quenching oils and insulating oils. The latter encompass a wide variety of products, including transformer oils, cable oils, condenser oils and switch gear oils.

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Chapter 9
Formulation of Automotive Lubricants

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Abstract The formulation of lubricants for current light- and heavy-duty vehicles (passenger cars and trucks) and also motorcycles/small engines is described in terms of engine types and meeting European, US and Japanese emission control requirements. Trends in the formulation of lubricants are discussed and the importance of high and low 'SAPS' for future developments emphasised. Specification and evaluation of lubricant performance for light-vehicle gasoline and diesel, and also heavy-duty diesel engines are described. Emphasis is given to diesel engine cleanliness by soot and deposit control and the effect of emission controls on lubricant formulation. The lubricant requirements for motorcycle and small engines, primarily two-stroke cycle, and their specifications are described.

9.1 Introduction

This chapter discusses the main influences on current and future light-duty (passenger) and heavy-duty (truck) vehicle engine oils and also small engines for motorcycles/light appliances in terms of engine design, emissions and fuel economy. This is followed by a detailed discussion of lubricant composition and performance assessment.

9.2 Passenger Car Engine Oils

9.2.1 Passenger Car Engine Types

Internal combustion engines, ICEs, for light vehicles can be divided into two main types, gasoline and diesel, although other types of engine are emerging. The gasoline engine still dominates most light-vehicle markets today, although diesel popularity in Europe now accounts for more than 50% of new light-vehicle sales.

Diesel and gasoline engines share many similarities in their mode of operation and in their component parts. However, there are some important differences that ultimately impact on their lubricant requirements, namely the fuel used, mode

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of ignition, temperature of combustion, exhaust gas composition and the resulting combustion products. The soot produced during diesel combustion is at the heart of the differences in the lubrication requirements between gasoline and diesel vehicles, and this soot also affects exhaust emission handling.

Liquefied petroleum gas, LPG, and compressed natural gas, CNG, are increasingly used as passenger car vehicle fuels predominantly in urban areas and driven by air quality concerns. However, relative to gasoline and diesel their use is still limited, and the passenger car engine technologies used have similar lubricant appetites to a standard gasoline engine. Therefore, LPG/CNG engine lubrication will not be considered separately here.

Homogenous charge compression ignition, HCCI, is an emerging combustion technology which operates at low temperature. Unlike standard diesel compression ignition, where the air/fuel charge is essentially stratified, HCCI utilises compression ignition of a well-mixed air fuel charge. Most of today's engine prototypes can sustain HCCI combustion only at low to medium loads. The advantages of HCCI are the ultra-low nitrogen oxides, NO_x, and particulate emissions, although hydrocarbon and carbon monoxide emissions can be higher than in conventional diesel combustion. Over the next 10–15 years, it is expected that HCCI will form a large part of the diesel fleet.

Hybrid light-duty vehicles are currently increasing their market share with new car sales in some markets expected to reach 10% by ca. 2010. Whilst this is a rapid penetration of new car sales, the rate of impact on the total global car parc will decline due to the relatively slow turnover of vehicles and the fact that most hybrids are sold into the developed world at present. Hybrids combine an internal combustion engine with an electric power train and batteries and are more energy efficient than an internal combustion engine alone. The internal combustion engine may be any of the types mentioned previously, and dependent on the type of hybrid, the combustion engine may run continuously or intermittently. For the latter case, stop/start running may present an additional challenge for the lubricant as the time taken to reach operating temperature and maximum protection may be longer.

9.2.2 Passenger Car Trends and Emission Legislation

The engine segment has classically been driven by targets set by the Original Equipment Manufacturers, OEMs, including such targets as fuel economy, longer lubricant drain intervals, engine durability and cost of ownership. These targets attempt to simultaneously meet the needs of vehicle manufacturers, vehicle owners and government legislators.

In recent decades, the OEM requirements have been supplemented by the need to meet government vehicle emission legislation. Future legislation will penalise the sale of vehicles that do not meet the fuel economy and emission standards of the time. As a general principle, this requirement applies globally, but there are regional variations in these aspirational targets. Air quality has historically been the main driver in both North America and Europe, and all engine manufacturers are required by legislation to meet targets for emissions of CO, NO_x, particulates and hydrocarbons. Additionally in America, OEMs are required to meet Corporate Average Fuel Economy (CAFE), targets or face stiff financial penalties.

European emission requirements: Since the introduction of the Euro 1 standard in 1992 to today's Euro 4 standard, European emissions legislation has reduced light-vehicle diesel pollution from the combined emissions of CO, NO_x, hydrocarbons and particulate matter by 82%, Fig. 9.1. Within the same timeframe, CO_2 emissions have been reduced by 25%. Further cuts are targeted with draft specifications for Euro 5 and Euro 6. For passenger car diesel engine emissions:

- Euro 1 targets were achieved by the introduction of intercoolers and turbochargers,
- Euro 2 targets were achieved by the introduction of cleaner fuel, e.g. low sulphur diesel,
- Euro 3 targets were achieved by the introduction of retarded injection timing and piston design changes,
- Euro 4 targets were achieved through the introduction of diesel particulate filters on commercial vehicles and also on many passenger car vehicles.

Within the same timeframe, light-vehicle gasoline emissions have been reduced by 74%, and Euro 5 and Euro 6 will introduce limits on particulate matter emissions from gasoline engines, Fig. 9.1. For passenger car gasoline engine emissions:

- Euro 1 targets were achieved via single-point fuel injection and the use of three-way catalysts,
- Euro 2 targets were achieved via multipoint fuel injection and three-way catalysts;
- Euro 3 targets required the introduction of sequential multipoint fuel injection and three-way catalysts,
- Euro 4 targets required the introduction of sequential multipoint fuel injection and starter three-way catalysts.

Diesel fuel sulphur content trending down to zero also has had a positive impact.

New European legislation means that OEMs will be fined for CO_2 emissions above the target of 120 g CO_2/km. From 2012 the fine is proposed at €20 per g CO_2/km, rising to €95 per g CO_2/km by 2015. To meet these fuel economy and emissions targets, new hardware technologies are required. For gasoline vehicles, new hardware technologies have been required, including gasoline direct injection (GDI), NO_x storage catalysts and variable valve timing. Diesel engine technologies

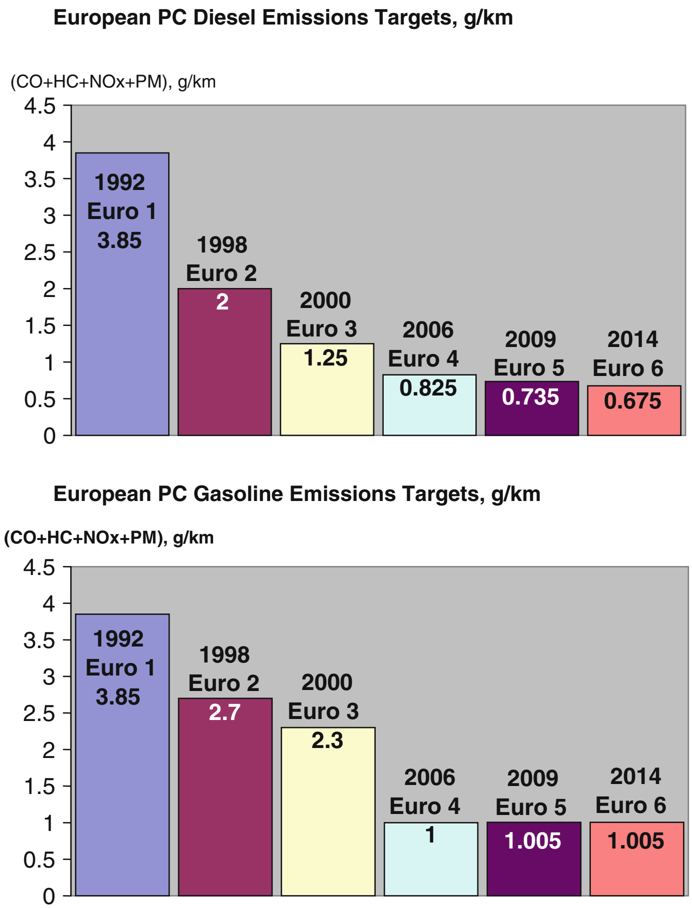


Fig. 9.1 European emissions regulations and reductions since 1992. Values given indicate total combined emissions (CO + hydrocarbons + NO_x + particulate matter) in g/km

are moving to direct injection (DI), NO_x storage catalysts and diesel particulate filters (DPFs).

Euro 4 limits on diesel particulate matter necessitated the use of diesel particulate filters on some vehicles, highly efficient exhaust after-treatment filters which remove harmful particulate emissions, even down to ca. 10 nm. One consequence is that the engine lubricant is required to be compatible with the DPF, ensuring that the device functions correctly and efficiently, not only over the complete service interval but for the lifetime of the system. The DPF compatible lubricant is still required to meet all of the traditional performance targets and remain cost effective.

North American emission requirements: Two sets of US Federal emission standards are defined for cars and light-duty trucks, Tier 1 and Tier 2. Tier 1 requirements were published in 1991 and fully implemented in 1997. Tier 2 standards were adopted in 1999 and began to be phased in commencing in 2004. The emission targets for each vehicle depend upon its weight and service type.

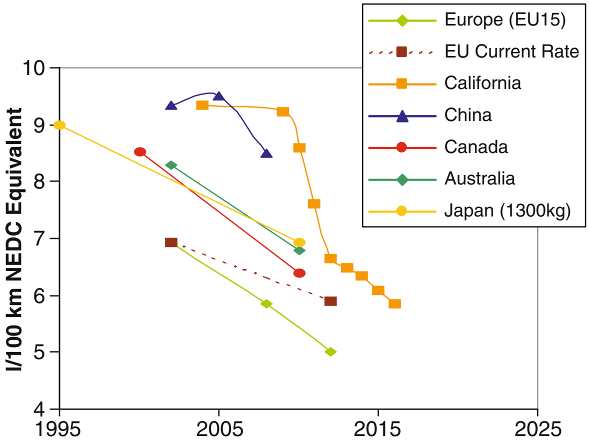
Federal Tier 1 emission standards apply to a vehicle life of 100,000 miles. NO_x limits for diesel engines are less stringent than for gasoline. Emissions are measured over the Federal Test Procedure, FTP75, and are expressed in grams/mile.

Federal Tier 2 emission standards bring further reductions to the targets defined in Tier 1. In addition to tighter emission limits, Tier 2 introduces a number of important changes that make compliance with the standard more difficult for larger vehicles. Because of the tighter targets, larger engines such as those used in light trucks or SUVs will have to use more advanced emission control technologies than smaller engines. The same emission limits apply to all engines, irrespective of the fuel used, that is, vehicles fuelled by gasoline, diesel or alternative fuels all must meet the same standards. Tier 2 also introduced new requirements for fuel quality. As in Europe, cleaner fuels will be required by advanced emission after-treatment devices, e.g. catalysts, that are needed to meet the regulations. Sulphur levels in gasoline and diesel fuel quality are targeted.

Legislative trends – air quality and carbon emissions: Existing exhaust after-treatment technology has already enabled more than a 90% reduction in emissions related to local air quality. The future challenge is to improve fuel economy and reduce carbon dioxide emission levels. The developed world has fuel economy/CO_2 targets for the end of the decade and beyond, and OEMs will have to meet these targets as an average across their fleets. However, when combined, these improvements will require further drivetrain friction reductions, aerodynamic improvements, reduction in tyre rolling resistance, etc. Engine hardware will also evolve, for example engine downsizing, increased exhaust gas recirculation, more turbo/supercharging and advanced fuel injection systems. However, even when combined, these improvements are not expected to achieve the new emissions targets and consequently OEMs will have to develop new power-plant technologies. Increasing emphasis on vehicles with significantly reduced emissions will lead to a variety of new, competing technologies. Examples being considered include electric vehicles, hydrogen internal combustion, homogenous charge compression ignition (HCCI) and carbon-neutral biofuels. With the exception of fully electric vehicles, all of these new technologies will require lubricants tailored to the application.

Individual regions use different measurements for fuel consumption or CO_2 targets – for example, the United States uses a fuel economy measurement in miles per gallon whilst Europe uses tailpipe emissions of CO_2 in g/km. These targets can be compared if they are calculated on an equivalent basis as litres fuel/100 km driven, as in Fig. 9.2.

Fig. 9.2 Current and future CO_2 emission targets for different regions, on the equivalent basis of litres fuel/100 km driven



9.2.3 *Formulation and Functions of a Passenger Car Engine Oil (PCEO)*

Passenger car or light-vehicle lubricants are usually formulated either as dedicated gasoline products or, alternatively, for combined passenger car diesel and gasoline service. Whilst there are some similarities in performance requirements for passenger car diesel and gasoline lubricants, there are also some key differences. In both engine types, the lubricant has to protect against wear and oxidation and neutralise harmful acids. In addition, the fluid viscosity is critical in providing hydrodynamic separation in the bearings and hydraulic pressure in key components, such as valve adjusters.

The key differences between the gasoline and diesel engines are that gasoline engines require protection against black sludge, see Section 9.3.5, whereas diesel engines require protection against high-temperature piston deposits and the dispersion of soot particles generated by the diesel combustion process. Additionally, the viscosity increase of a diesel lubricant resulting from soot ingress needs to be controlled. A modern multi-grade engine lubricant will contain the following components:

- Base oil – can be mineral, synthetic or a mixture of these,
- Additive system – contains dispersants, detergents, antioxidants, antiwear agents, antifoam, corrosion inhibitors, plus other ‘compatibility agents’ for elastomers,
- Viscosity modifier – polymer added to reduce the change in viscosity with temperature.

The relative amounts of these components are dependent upon the application, the viscosity grade and the regional performance demand. The key functions of the lubricant and the specific additives used to deliver these functions are described in the following subsections.

Wear: There are two broad types of mechanical wear:

- two-body wear – where primary engine components come in contact with each other,
- three-body wear – when a foreign body, e.g. swarf, soot or another solid contaminant, enters the interface between two primary engine components.

In both cases, damage to the primary engine components leads to decreased engine performance and, ultimately, component failure. The engine components are affected the most where contact stresses are high, as described by the Stribeck Curve in Chapters 3 and 8. For example, the most critical areas are the valvetrain, piston rings and piston liners. Soot-related timing chain wear is also a key parameter for diesel engines in particular.

Two-body wear can be controlled by the addition of antiwear additives such as ZDDP. Three-body wear is additionally controlled by dispersants and detergents. Preventing the introduction of third bodies, e.g. via contamination through air ingestion or through creation of wear particles, is also important.

Oxidation: Oxidation of the lubricant basestock leads to viscosity increase and consequent issues of pumpability, fuel economy and ultimately oil starvation. Oxidation products also include organic acids which can cause corrosion and deposits around the engine but particularly in the cooler parts of the engine, discussed previously in detail in Chapters 4 and 7. Dedicated antioxidants such as phenols and amines are used to control oil oxidation, and the antiwear agent ZDDP also acts as a powerful antioxidant.

Acid neutralisation: As mentioned above, acids are produced by oxidation as well as by fuel combustion. Fuel sulphur levels are decreasing in the developed world to enable after-treatment devices to function properly. This reduction is also reducing the formation of sulphurous acids which affect both engine and environment. In the developing world, lubricants may still need to cope with very high fuel sulphur levels of the order of >3000 ppm sulphur. Acid neutralisation is given by addition of basicity in the form of overbased detergents and, to a lesser degree, by dispersants.

Black sludge: Black sludge is a soft grease-like deposit which can be wiped from engine component surfaces. Black sludge formation results from complex interactions between lubricant, fuel and combustion by-products and is heavily influenced by engine design, climate, drive cycle, oil drain interval and local fuel quality. Outbreaks of sludge formation are often sporadic and localised so identifying the root cause can be extremely difficult. Black sludge generates deposits around the engine, including the sump and valvedeck. If the sludge blocks the oil pick-up pipe, then the resulting oil starvation causes catastrophic damage to the engine. Black sludge protection is provided primarily by dispersants and, to a lesser extent, antioxidants.

Piston deposits: In comparison with black sludge, these are high-temperature deposits formed in the ring grooves and on the piston crown, skirts, lands and undercrown. Piston deposits, particularly in the ring grooves, cause the piston rings to ‘stick’ in position, which increases combustion gas blow-by and ultimately leads to bore polishing and engine failure. This is particularly true for modern diesel engines where high combustion temperatures mean that deposits form on the piston.

Piston deposit formation is strongly influenced by the type of base oil used and also by the selection and content of viscosity modifier. Detergent and dispersant selection also have significant effects on reducing the formation of piston deposits.

Soot dispersion: Soot particles formed during the diesel combustion process can cause three-body wear in the engine and must be dispersed to prevent this happening. Soot is suspended in the oil by dispersants, which minimises the effect of soot on wear.

Soot-induced viscosity control: Lubricants with high levels of soot, e.g. more than 3% by mass, can show dramatic increases in viscosity. Oil formulations must control this viscosity increase and maintain its function in the engine when it contains soot. Soot-induced viscosity control is influenced by dispersant type and level.

Regional performance demand: Different geographical regions have different market requirements. European oils tend to be for longer drain applications, up to 30,000 miles between oil drains, whereas North American market lubricants tend to be changed every 3000–10,000 miles. Additionally, differences between 'developed' and 'developing' markets have an effect on the required lubricant performance and hence the formulation and the lubricant drain interval. Local fuel variation also needs to be considered, e.g. the sulphur content of diesel, overall fuel quality based upon refinery processing and contamination of fuel.

High levels of fuel sulphur lead to higher levels of sulphurous acids in the combustion products and therefore lead to faster depletion of the lubricant's acid neutralising properties. Fuel quality around the world is improving but not at the same rate or to the same levels. These differences must be taken into account when specifying appropriate lubricant formulations in different regions. Poor base fuel quality has a detrimental impact on engine deposits and oxidation control. Fuel contamination gives a variety of problems, dependent upon the nature of the impurity, ranging from contamination by water to tar fractions.

9.2.4 Lubricant Formulation Trends

Before 2001, the components used for specific lubricant functions had remained relatively consistent since the introduction of ashless dispersant technology in the 1960s. However, recently introduced emissions legislation mandates the use of exhaust after-treatment for both gasoline and diesel light vehicles in many parts of the developed world, and this requirement affects component selection for modern formulations.

Three-way catalysts are used in gasoline cars to control the emissions of hydrocarbons, carbon monoxide and nitrogen oxides. Oxidation catalysts and diesel particulate filters, DPFs, are used in diesel vehicles to control the emissions of soot particles, hydrocarbons, carbon monoxide and nitrogen oxides. All of these after-treatment devices are sensitive to additive components of the lubricant. Three-way catalysts are permanently poisoned by the action of sulphur and phosphorus reacting with, and penetrating through, the metallic surface washcoat, thus deactivating the catalyst. Ash-forming additives such as ZDDP and detergents physically block the DPF, eventually affecting gas flows and engine performance.

Evolution in emissions legislation, engine hardware and exhaust after-treatment is driving a fundamental change in lubricant formulation. The latest OEM and industry specifications and requirements mandate lower concentrations of *S*ulphated *A*sh, *P*hosphorus and *S*ulphur in the lubricant, the so-called mid and low '*SAPS*' oils. Whilst these new lubricant formulations represent the cutting edge of the industry and are required for the newest powertrains, the majority of vehicles in the car parc are not brand new and the older vehicles do not require the most modern formulation technology. First, a traditional 'full SAPS' technology is considered.

A typical 'Full SAPS' passenger car engine lubricant: Table 9.1 shows typical lubricant components from two different markets, and Table 9.2 shows a typical additive package composition. Each of these additive components contains an amount of diluent oil that aids manufacture, handling and blending.

Table 9.1 Composition of a typical 'full SAPS' engine lubricant

	European lubricant for gasoline + diesel	North American lubricant for gasoline only
Component	Typical content (mass%)	Typical content (mass%)
Base oil	78	85
Additive package	12	8
Viscosity modifier[1]	10	7

[1] Viscosity modifier as a concentrated solution in base oil

Table 9.2 Composition of a typical additive pack

Component	Function	European gasoline and diesel additive package (mass%)	North American gasoline additive package (mass%)
Ashless dispersant	Soot and sludge handling	60	48
Detergent	Piston cleanliness, corrosion inhibition and acid control	25	28
ZDDP antiwear	Wear and oxidation control	10	14
Antioxidants	Oxidation control	3	7
Others	Antifoam, corrosion inhibition, supplemental antiwear and friction modifiers	2	3

'Low SAPS' engine oil technologies: Low SAPS technologies are being introduced primarily in markets with both a high-diesel population and high-quality diesel fuel. Legislators in markets with high-diesel populations have driven diesel fuel quality to higher levels. That same legislation is now driving reduced tailpipe

emissions via after-treatment devices such as diesel particulate filters. These filters can be blocked by metallic ash formed from oil burned during the combustion process. As a consequence of the introduction of DPFs, modern formulations are now using less of traditional ash-containing components. Ash for oils is measured by a standard method known as 'Sulphated Ash' via the ASTM D874 procedure. The main changes between full SAPS and mid/low SAPS formulations are described below.

The use of metal-containing additives is becoming restricted, with knock-on effects over the whole lubricant formulation. Using ash-containing detergents such as the overbased calcium and magnesium salts of sulphonates, phenates and salicylates is now restricted by their ash content. With restrictions on the amount of ash-forming components, a balance has to be struck between detergents and the amount of ZDDP antiwear, which also contains ash. ZDDP also has a major effect on the lubricant's phosphorus and sulphur content. These formulation restrictions have a large impact on the lubricant's performance, and the replacements for these additives are generally less effective and can introduce performance compromises and conflicts. Examples of the latest high, mid and low SAPS specifications from Europe, North America and selected OEMs are shown in Table 9.3.

Table 9.3 High, medium and low SAPS, from Europe, North America and some OEMs

Industry body/OEM	Specification	Sulphated ash (mass%)	Phosphorus (mass%)	Sulphur (mass%)
ACEA	A1/B1-04	≤1.3	Report	Report
ACEA	A3/B3-04	≤1.5	Report	Report
ACEA	A3/B4-04	≤1.6	Report	Report
ACEA	A5/B5-04	≤1.6	Report	Report
ACEA	C1-04	≤0.5	≤0.05	≤0.2
ACEA	C2-04	≤0.8	0.070–0.090	≤0.3
ACEA	C3-04	≤0.8	0.070–0.090	≤0.3
API	GF-4		0.06–0.08	≤0.5 (≤0.7 10W-xx)
API	SM		0.06–0.08	0.5 (0.7 10W-xx)
BMW	LL-04	0.63–0.8	≤0.08	≤0.2
Daimler	MB p229.31/51	≤0.8	≤0.08	≤0.4
Ford	WSS-M2C934-A	≤0.5	≤0.05	≤0.2
PSA	TBC	≤0.8	≤0.08	≤0.4
Volkswagen	TL52195 VW504/507	(1)	(1)	(1)

Notes: (1) VW ash, phosphorus and sulphur limits set by DPF blocking test, not chemical limit.

Reduced detergent levels can be supplemented by adding ashless dispersants to deliver the necessary piston cleanliness. But the dispersant's high contribution to viscosity means that compromises have to be made elsewhere in the formulation. Dispersants, for example, have a detrimental effect on fuel economy and may lead to restricted choices of basestock and viscosity modifier to meet viscometric requirements. Furthermore, the high active nitrogen content that makes dispersants effective can also cause problems with elastomer compatibility.

ZDDP functioning as an antiwear additive can be replaced in part by molybdenum- and/or boron-containing components which are more ash treat-efficient but less cost effective. These replacements also provide less effective antioxidant function than ZDDP.

ZDDP functioning as an antioxidant can be replaced by ashless antioxidant components, such as hindered phenols and amines. Whilst effective, they are more expensive than ZDDP and can also compromise elastomer compatibility. Additionally, depending on the level of ashless antioxidant in the formulation, their use may mean that product material safety labelling is more alarming to the end consumer.

Over and above the performance considerations, these formulation changes also affect the cost of the formulation. For example, ZDDP is currently considered to be the most cost-effective antioxidant and antiwear additive component available, and alternatives are currently more expensive. Table 9.4 shows the composition of a typical low SAPS additive package.

Table 9.4 Composition of a typical European gasoline and diesel low SAPS additive package

Component	Function	European gasoline + diesel additive package (mass%)
Ashless dispersant*	Soot and sludge handling	70
Detergent	Piston cleanliness, corrosion inhibition and acid control	15
ZDDP antiwear	Wear and oxidation control	5
Antioxidants	Oxidation control	8
Others	Antifoam, corrosion inhibition, supplemental antiwear (e.g. B, Mo) and friction modifiers	2

*In addition to dispersant levels being higher than in the full SAPS case, there has also been a shift to using dispersants of higher performance activity.

9.2.5 Passenger Car Lubricant Specifications and Evaluating Lubricant Performance

Lubricant specifications: The required performance of a lubricant in a specific application is defined by a specification. For passenger car oils, the specifications are normally set by a regional industry body such as API, ACEA, JASO or by a vehicle manufacturer such as Ford, VW, Mercedes Benz. In some other applications, such as heavy-duty lubricants and transmissions, specifications may also be set by a military organisation or by a Tier 1 supplier to the vehicle manufacturer. Irrespective of the organisation defining the specification, there are common areas against which the passenger car lubricant will be measured.

Passenger car lubricant performance evaluation: Specifications usually contain a mixture of physical/chemical requirements and performance properties. Physical/chemical limits include viscosity at multiple temperatures, volatility, pour point and limits on chemical components such as phosphorus and chlorine. The performance requirements may comprise some, or all, of the following:

- bench tests – for example, a glassware test for oxidation.
- rig tests – where the lubricant performance in a specific area can be examined without the complications of fuel dilution or combustion products, etc. For example, a wear test which uses real engine components but is driven by an electric motor rather than a fired engine.
- fired engine tests – these are also usually targeted at a specific performance parameter, but unlike rig tests use the full engine operating under fired conditions. The engine will normally be fitted with a dynamometer and run on a fixed test stand in a laboratory.
- chassis dynamometer – in which a vehicle is driven on a rolling road, quite common for fuel economy tests.
- field trials – in which the lubricant is evaluated in cars driven on the road. Field trials provide the final proof of performance in the 'real world' indicated through the previous engine and rig tests.

Most tests are designed to represent use in the field, which may mean an oil lifetime of 3000–30,000 miles (5000–50,000 km). To demonstrate such performance in an acceptable timescale, the tests may be carried out in a way which is more severe than in-field use. Examples of how engine tests are made more severe include the choice of fuel, extremes of operating temperature (high or low), engine speed/load, use of specific engine components and restrictions in oil top-up during test. Methods of increasing the severity of bench tests include temperature, catalysts and addition of acid or water, etc. The following subsections describe the most common performance evaluations.

Oxidation: During the combustion process, free radicals are formed which can degrade the oil via oxidation, generally observed as a viscosity increase. If an oil becomes too viscous, it cannot be pumped to where it is required and thus the engine is starved of oil. Engine tests for oxidation are made more severe via extended high-temperature operation, increased blow-by and no oil top-up.

Valvetrain Wear: Wear tests measure the oil's ability to protect the valvetrain (camshaft, tappets, etc.) from wear. Engine components may be either visually inspected or physically measured at the end of the test. The results are then either expressed as a rating, e.g. for scuffing, or reported in 'microns wear'. Engine tests for wear are made more severe by the use of low-temperature operation, extended dynamic loading and even operating with higher spring forces. Some tests use radioactivity techniques to monitor wear rates in real time as well as absolute wear levels at the end of the test.

Gasoline Sludge: Even the most modern of gasoline engines can suffer from black sludge when fuel quality is poor, e.g. in emerging markets. Engine oils are required to protect the engine against sludge build-up, which manifests itself as deposits, oil pressure increase and even catastrophic engine failure. Sludge tests routinely use special poor quality fuel and low-temperature phases of operation. Sludge is assessed through visual rating of engine cleanliness, its physical depth and coverage of sludge and also oil filter pressure.

Fuel Economy: The fuel economy benefit of lubricants is an important part of many specifications, such as ILSAC, reflecting the legislative requirements in the United States (CAFE), and Europe also requires lubricants to provide a fuel economy benefit. The fuel efficiency of the candidate oil is evaluated by measuring the fuel consumed by the engine running a specified duty cycle versus a reference oil. The operating conditions selected, the starting temperature, speeds and loads, etc., have a large effect on engine fuel consumption, and these test conditions vary between specifications. The test may use an engine running on a test stand, or alternatively use the whole vehicle running on a rolling road (chassis dynamometer).

Diesel Engine Cleanliness: In many regions, diesel powered vehicles are an important segment of the car parc. Diesel engines have their own special requirements in addition to the gasoline performance requirements; the chief amongst these is diesel engine cleanliness. In particular, piston cleanliness and ring sticking need to be controlled. Piston cleanliness tests may use lower quality fuel and cyclic hot/cold duty engine cycles to increase test severity.

Diesel Soot Handling: The diesel combustion cycle produces soot from incomplete fuel combustion. The soot loading of a lubricant can lead to an increased oil viscosity and hence the lubricant is required to maintain an acceptable viscometric profile even when loaded with soot. Soot loading of a lubricant to verify its soot-dispersing capability can be achieved by altering the injection timing of the engine, giving poorer combustion and hence soot production. The lubricant's performance is evaluated by measuring the viscosity of the sooted oil relative to a reference test.

Materials Compatibility: Finally, any lubricant is required to be compatible with non-metallic components used in the engine, such as plastics, resins and elastomers. In particular, polymeric materials used in seals and plastics need to retain their integrity when in contact with the lubricant. ACEA and most OEMs have material compatibility tests to ensure that the lubricant will not cause undue degradation in key physical parameters of the polymer. These parameters include tensile strength, hardness, volume and crack formation. Any such loss of polymer integrity could be manifest as oil seal leaks or in more extreme cases as a blown gasket. Current engine test examples for American, European and selected OEM specifications are shown in Table 9.5.

Other aspects of passenger lubricant evaluation: In addition to the engine performance of the lubricant, there are other aspects that require consideration before

Table 9.5 Current American, European and selected OEM engine tests

Test type	ACEA example	API example	OEM example(s)
High temperature deposits, ring sticking and oil thickening	TU5JP-L4 (CEC-L-88-T-02)	Sequence IIIG	VW T4 (PV1449) Opel OP1 BMW M54
Low temperature sludge	Sequence VG (ASTM D6593-00)	Sequence VG (ASTM D6593)	
Valvetrain scuffing wear	TU3M (CEC-L-38-A-94)	Sequence IVA (ASTM D6891)	VW cam and tappet (PV5106) Opel cam and tappet (GMI-L-6X01-4/99)
Black sludge	M111SL (CEC-L-53-T-95)		
Fuel economy	M111FE (CEC-L-54-T-96)	Sequence VIB (ASTM D6837)	VW 1.8T (PV1451) Opel fuel economy (GME8331TP)
Ring sticking and piston cleanliness	VW 1.6 TC D (CEC-L-46-T-93)		Opel DI Test (MOD-D001)
Medium temperature dispersivity	XUD11BTE (CEC-L-56-T-98) Or DV4 (CEC-L-093)		
Wear, viscosity and oil consumption	OM602A (CEC-L-51-A-98)		Mercedes Benz OM611LA
Direct injection diesel piston cleanliness and ring sticking	VW TDi (CEC-L-78-T-99)		
Bearing weight loss		Sequence VIII (ASTM D6709)	
Diesel valvetrain wear			VW RNT (PV1473) BMW N42 RNT Opel RNT (GME8330TP)
Oil/elastomer compatibility	ACEA Seals (CEC-L-39-T-96)		VW Seals (PV3344) DC Seals Opel Seals (GME50255)

a formulation can be commercialised. The lubricant formulator must be cognisant of the conditions that occur during manufacture, storage and application. Lubricants are meta-stable at low temperatures, and the polymeric components have a tendency to separate out. This is particularly likely to occur where cooling rates are low, e.g. in drums or tanks stored in unheated areas. The lubricant must be compatible with other lubricants with which it may be reasonably expected to mix with in the engine. The major source for this is topping up of the oil with other lubricants. Such a mixture must maintain its integrity in the engine and perform satisfactorily under all normal driving conditions. Such stability and compatibility performance is covered within some specifications, such as API SJ and above.

9.3 Heavy-Duty Diesel Engine Oils

9.3.1 Introduction

Heavy-duty diesel engine lubricants are sufficiently different from the lubricants for gasoline and diesel light vehicles that they justify a separate section. The issues to be addressed here are:

- heavy-duty diesel trends and emission legislation,
- engine strategies to reduce emissions and impact on engine oil formulation,
- heavy-duty diesel engine oil specifications for the United States, Europe, Japan and ROW.

9.3.2 Heavy-Duty Trends and Emission Legislation

In general, emission legislation continues to drive hardware development in the automotive industry. In future, global legislation will mandate progressively tighter limits for NO_x, particulates and CO_2. This is forcing OEMs to make significant advances in engine and exhaust after-treatment technology to meet the legislated exhaust emission requirements. This is further complicated since there is no harmonisation of current global emissions standards: Fig. 9.3 shows the state of the heavy-duty legislated emissions requirements around the world.

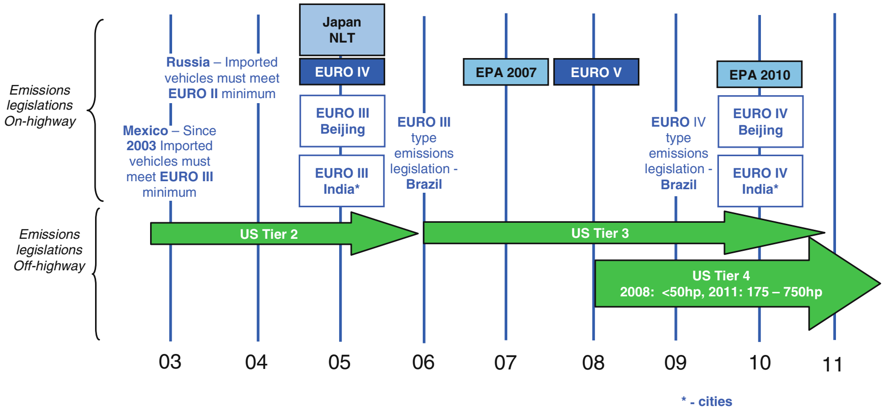


Fig. 9.3 Heavy-duty diesel emissions regulations for various countries

Details of the ‘on-highway’ emissions legislation in various parts of the world are given in Tables 9.6a–c. Many countries in emerging markets are using the Euro legislation to set their emissions limits, phasing them in a few years after they are implemented in Europe. ‘Off-highway’ limits are also being tightened and, again, these tend to lag behind the ‘on-highway’ limits.

Table 9.6 EU, US and Japan emission standards for heavy-duty diesel engines (note different measurement standards)

(a) EU emission standards for HD diesel engines, g/kWh

Tier	Category date	CO	HC	NO_x	Pm
Euro III	Oct-2000	2.1	0.66	5.0	0.10
Euro IV	Oct-2005	1.5	0.46	3.5	0.02
Euro V	Oct-2008	1.5	0.46	2.0	0.02

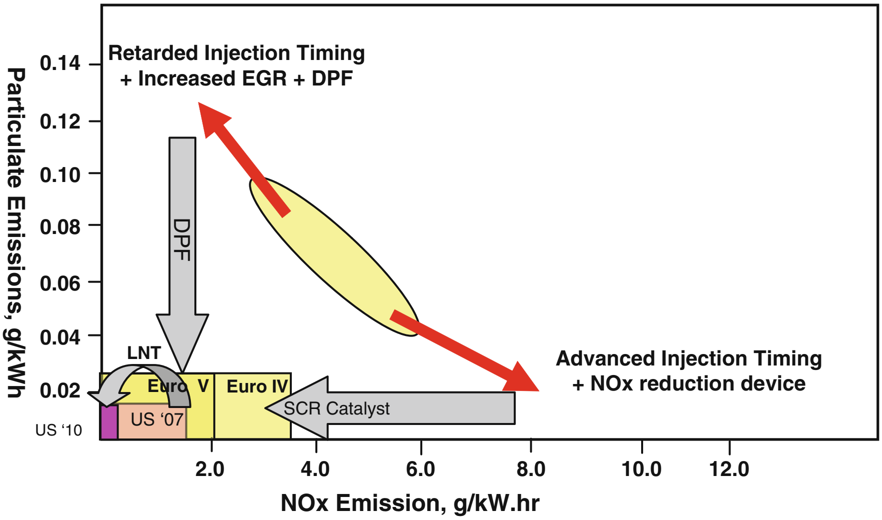
(b) Emission standards for US Trucks, g/bhp h

Year	CO	HC	NO_x	NMHC	Pm
1998	15.5	1.3	4.0	–	0.1
2002 (2004)	15.5	1.3	2.0	0.5	0.1
2007	15.5	1.3	1.1	0.14	0.01
2010	15.5	1.3	0.2	0.14	0.01

(c) Emission standards for Japan, g/kWh, GVW >2500 kg (>3500 kg from 2005)

Year	CO	HC	NO_x	Pm
2003 (new short-term emissions)	2.22	0.87	3.38	0.18
2005 (new long-term emissions)	2.22	0.17	2	0.027

Introduction of new, tighter, emissions regulations require modifications to the engine and/or the addition of exhaust after-treatment to clean up engine-out emissions. The effect of these changes on the engine oil can be either negligible or quite significant. Fig. 9.4 shows how heavy-duty OEMs may try to reach the emission standards.



DPF = Diesel Particulate Filter
EGR = Exhaust Gas Recirculation
SCR = Selective Catalytic Reduction
LNT = Lean NOx Trap

Fig. 9.4 After-treatment technologies to meet exhaust emission standards

9.3.3 Heavy-Duty Engine Strategies Applied to Reduce Exhaust Emissions

The following sections give more detail of the engine technologies being applied to reduce diesel exhaust emissions and of their potential impact on the engine oil. Technologies used to control emissions will include some of the following:

- air charging,
- fuel injection equipment,
- valve configuration,
- exhaust gas recirculation, EGR,
- exhaust after-treatment,
- piston assembly,
- fuel quality.

Air Charging: Turbocharging boosts the volume of air taken into the engine to increase engine efficiency and reduce emissions. Turbochargers have been optimised to give variable boost pressure across the engine speed and load map. This has been achieved in more recent engine technologies by using a variable geometry turbocharger, VGT, sequential turbocharging or a waste gate turbocharger. The last approach, whilst still effective, is less efficient compared to the previous two. Charge air cooling using an intercooler has also been optimised to give appropriate cooling of the turbocharger air.

Turbocharger boost pressures are increasing to improve engine efficiency and increase power which, in turn, leads to higher boost air temperatures. In some cases, charge air temperatures exiting the turbocharger can be greater than 200°C, not a major issue for the lubricant except where the engine blow-by gas is re-circulated back through the turbocharger into the engine. There is the possibility for oil mist in the blow-by gas to form deposits when the turbocharger boost temperature is high. Deposits can form in the turbocharger itself or further downstream in the intercooler. When the deposits are sufficiently heavy, the turbocharger efficiency may drop, leading to a loss in engine power, requiring the turbocharger to be cleaned or replaced.

European lubricant specifications require some turbocharger deposit assessment. This is measured in the Mercedes Benz OM 441LA engine test for the ACEA heavy-duty diesel oil sequences and/or the DIN 51535 glassware deposit test for some specific European OEM specifications. Both of these tests assess the lubricant's ability to withstand high turbocharger temperatures without coking the oil. In the OM441LA engine test, the drop in turbocharger boost pressure over the 400 h test is measured. For the DIN 51535 test, the glass tube deposits after 3 h at 310°C are weighed. It is not absolutely clear what causes turbocharger deposits, but some evidence suggests that polymeric viscosity modifiers, used to formulate multi-grade lubricants, can exacerbate deposit formation at elevated turbocharger temperatures. Reducing the level of viscosity modifier can help in reducing the turbocharger deposits, at least when they are measured in the above two tests. The most common grade for heavy-duty engine oils is SAE 15W-40. Wider span viscosity grade oils, e.g. 10W-40, 5W-40 and 5W-30, formulated with low VI mineral oils may cause problems. But in most heavy-duty diesel lubricants these 'wide-span' grades are formulated with high VI synthetic base oils which help minimise deposit formation. Additive formulation effects are more difficult to understand with respect to turbocharger coking. Some OEMs believe that high ash formulations give higher levels of deposits; therefore, it may be expected that the newer, lower SAPS formulations could give lower turbocharger deposits.

In Japan the 'Hot Surface Deposit Control Test', or Hot Tube Test as it is more commonly known, assesses turbocharger deposit control, designated JPI-5S-55-99. It runs for 16 h using glass tubes held at 280°C for both the JASO DH-1 and DH-2 engine oil specifications with the tubes rated for colour at the end of test against reference tubes. A dark-coloured tube indicates poor performance and a light-coloured tube better performance. Historically, the JASO Hot Tube Test favoured high ash formulations, but more modern lower SAPS formulations, as prescribed for JASO DH-2, are capable of passing the test.

To meet the US 2007 emissions standards, some OEMs re-circulate a portion of the engine blow-by gases back into the engine, in most cases by directing them upstream of the turbocharger. As of 2009, no test is currently available to measure turbocharger deposits in API CJ-4.

Fuel Injection Equipment: For many years, engine designers have used the diesel fuel injection system to modify diesel exhaust emissions. Injecting fuel later in the combustion cycle, 'retarding' as it is more commonly known, reduces NO_x

formation but increases the amount of particulates, as in Fig. 9.4. Retarding the fuel injection has been a common strategy to reduce NO_x emissions since the early 1990s. At the same time, advances in fuel combustion have further reduced particulate emissions.

Many fuel combustion improvements have resulted from new fuel injection systems; the most recent heavy-duty diesel engines technologies include the unit injector and common rail fuel injector. These fuel injection systems are used to deliver fuel more efficiently to the combustion chamber in several ways. The first is by using higher fuel injection pressures which improve fuel atomisation and thus combustion. The second is by using multiple injections within a cycle which allows the fuel injection event to be tailored to ensure a more controlled combustion. This controlled combustion ensures that particulate formation is reduced without the associated rise in NO_x. Use of a pilot fuel injection early in the combustion cycle enables the engine designer to minimise the rapid pressure increase associated with a single fuel injection. Pilot injection can be used to minimise emissions or to reduce noise, the main injection is then made close to Top Dead Centre to reduce particulate emissions. A post-fuel injection, late in the combustion cycle, can increase the exhaust gas temperature to regenerate a diesel particulate filter.

Reduction of diesel exhaust emissions has, in some cases, led to engines producing more soot within the lubricant, exacerbated by extended oil drain intervals leading to more soot-related wear. Some low-emission engines have also experienced increased fuel dilution, causing premature ageing of the lubricant. These issues have presented the lubricant formulator with an array of problems that must be addressed.

Modern oil formulations now contain high levels of ashless dispersants to keep the soot particles well dispersed. Antiwear additives, mainly ZDDP, have also been boosted to cope with the higher levels of abrasive soot wear.

Valve Configuration: To improve air delivery during the engine cycle, many modern engines use four valves per cylinder instead of two. Higher contact pressures may result from these more complex valvetrains which, combined with high soot levels, can cause valvetrain wear.

For the API CH-4 heavy-duty diesel lubricant specification in 1998, soot-related engine wear was assessed using the Cummins M11 HST (high soot test) and the 6.5 l Roller Follower Wear Test (RFWT). As EGR effects were introduced into the API CI-4 category in 2002, the Cummins M11 HST engine test was upgraded to the M11 EGR engine test. For API CJ-4 in 2007, the Cummins ISM test has replaced the M11 EGR, and the Cummins ISB test has been added to measure soot-related wear in a cam follower contact.

Lubricant formulations meeting API CG-4 standard and above have generally contained greater than 0.1% levels of phosphorus. Furthermore, as the soot levels in lubricants have increased so have the levels of ashless dispersants, typically exceeding 6%. It is believed that the additional dispersant helps to minimise wear by dispersing soot and contributing to the oil film thickness. Lubricants with lower detergent soap levels help to minimise soot wear, but this requirement needs to be balanced with keeping the piston clean, which tends to require higher levels of detergent soap. High levels of detergent soap can interfere with the phosphorus antiwear film.

European heavy-duty diesel valvetrain wear is currently assessed in the Mercedes Benz OM602A engine, a light-duty indirect diesel injection (IDI) engine that measures cam wear. More recently, the Mercedes Benz OM611 has been introduced as a requirement for all current MB specifications. The test has 18 different rated parameters with the limits being tiered for the various MB specification levels. As of 2009, a new test is just finishing development and will replace the OM602A in the MB and ACEA engine oil sequences. It will be designated the OM646LA and is a Euro 5 passenger car diesel engine.

In Japan, valve train wear is assessed in the Mitsubishi 4D34T4, a four-cylinder 3.9 l heavy-duty diesel engine. Cam nose wear is measured. The passing limit for JASO DH-1 and DH-2 is 95.0 μm maximum wear normalised to 4.5% soot. Tests carried out during the 1990s in Japan indicated that some API CG-4 oils did not meet this requirement, with wear rates greater than 200 μm being measured.

Exhaust Gas Recirculation (EGR): EGR, as its name implies, is a recirculation of exhaust gas back into the engine, where part of the exhaust gas is recycled back into the combustion chamber, displacing some of the fresh air charge. The result is that the temperature of combustion is lowered and the amount of NO_x in the exhaust reduced. The EGR gas is usually cooled prior to being introduced into the inlet manifold. The re-circulated exhaust gas may contain acidic combustion products which can have a harmful effect on the engine and the lubricant. Soot levels tend to be higher with EGR since the oxygen levels in the intake air are lower, and the increased acids and soot caused by the EGR have to be neutralised by the lubricant.

The API CI-4 category was primarily developed to meet the requirements of US 2002 engines using cooled EGR. Lubricants formulated for API CI-4 have the ability to neutralise acids and prevent wear with high levels of soot. In API CI-4 lubricants, the dispersant, antioxidant and antiwear levels are higher than typical API CH-4 lubricants. API CI-4 lubricants typically use high-quality Gp I or II base oils due to their oxidative stability.

In future the use of EGR is expected to increase for certain applications, particularly those which do not use Selective Catalytic Reduction NO_x after-treatment. When this happens, the levels of acids entering the lubricant via the blow-by gases may increase. Because of this, there is an expectation that drain intervals may need to be lowered if the base number of the lubricant drops too quickly. To counter this, reductions in fuel sulphur will help offset the increased levels of EGR and may allow lubricant drain intervals to be maintained. A good example is in North America where higher cooled EGR rates for US 2007 engines are used in combination with less than 15 ppm sulphur diesel. Maximum lubricant drain intervals have been maintained at around 25,000 miles (40,000 km).

In Europe, Scania and MAN are using EGR to meet Euro IV requirements for large heavy-duty trucks and are also proposing to use EGR to meet Euro V as well. Most other European OEMs are planning to use SCR to meet Euro IV and V standards. For lighter load applications, EGR and diesel particulate filters, DPF, will have to be used. Japanese OEMs are using EGR-DPF or SCR-DPF for the Japanese long-term emission regulations of 2005.

Exhaust After-Treatment: Advances in engine technology have given significant reductions in exhaust emissions within the engine. However, as the emissions targets are becoming more difficult to meet, it has been found that after-treatment technologies provide a useful way of reducing particulate and NO_x emissions. The four main after-treatment devices are:

- diesel oxidation catalysts, DOCs,
- diesel particulate filters, DPFs,
- NO_x adsorbers, lean NO_x traps, LNT,
- selective catalytic reduction, SCR, using urea or hydrocarbons.

Oxidation catalysts are useful for reducing hydrocarbons and the soluble organic portion of the diesel particulate, and they are widely used in both heavy-duty and light-duty diesel engines. To remove most of the particulate, which is required for JASO NLT 2005 and US 2007 regulations, a diesel particulate filter, DPF, is necessary. Dependent on how they are constructed, DPFs can filter out in excess of 99% of the carbonaceous portion of the particulate. At high exhaust temperatures, the trapped particulate in the filter is burnt off leaving a clean filter; however, at low exhaust temperatures, the un-burnt particulate will accumulate in the filter. It is necessary to burn off the accumulated particulate periodically, know as regenerating the DPF, otherwise the system back pressure will rise to unacceptable levels. There are various ways to ensure particulate burn-off at low exhaust temperatures. A common approach uses a Continuously Regenerating Trap, Johnson Matthey CRT^{TM}, with an oxidation catalyst prior to the DPF to generate more NO_2, a pro-oxidant, in the exhaust gas. The NO_2-rich exhaust gas will then burn the particulate at lower exhaust temperatures. An alternate approach injects fuel into the exhaust gas which ignites in the filter and generates sufficient heat to start a regeneration of the DPF. Some OEMs are using DPFs that are impregnated with a catalyst which is capable of reducing the regeneration temperature as well.

The main drawback to using a DPF is that over a long period of time, the system becomes blocked with ash from the oil and also engine debris. The ash blocking the DPF may necessitate that it is removed from the truck and cleaned, adding to running costs. To minimise this, OEMs and industry bodies are asking oil marketers to reduce the amount of ash-forming substances in the oil. This has led to *S*ulphated *A*sh, *P*hosphorus and *S*ulphur (SAPS) restrictions in some oil specifications. Table 9.7 details the heavy-duty SAPS requirements for Europe, United States and Japan:

Table 9.7 Heavy-duty SAPS requirements for the EU (ACEA), US (API) and Japan (JASO) as chemical limits for low-emission engines fitted with after-treatment

Specification Introduction	ACEA E6-04 Oct 2004	API CJ-4 Q4, 2006	JASO DH-2-05 2005
Sulphated ash, %	<1.0	<1.0	0.9–1.1
Phosphorus, %	<0.08	<0.12	<0.12
Sulphur, %	<0.3	<0.4	<0.5

NO_x reduction in diesel engines is more problematic since diesel exhaust usually contains an excess of oxygen making NO_x reduction very difficult. The simplest way to reduce NO_x is to introduce a reducing agent into the exhaust stream and then pass this over a catalyst with the exhaust gas, a process is called selective catalytic reduction (SCR). The reductant may be a hydrocarbon, or more commonly, ammonia or urea. SCR using urea is becoming the most popular method for heavy-duty OEMs in Europe to meet Euro IV and Euro V emissions standards. Since fuel injection may possibly be advanced with SCR, it is expected that this after-treatment strategy will not increase oil soot levels.

Piston Assemblies: Designs have had to evolve to meet the ever-increasing demands of more power and lower exhaust emissions. Piston design has had to change to cope with longer service life, higher fuel ignition pressures and lower exhaust emission requirements which not only has stressed the engine more but has a significant impact on lubricant composition. High lubricant temperatures are the main enemy, for when turbocharging was first applied piston temperatures increased as the charge air temperature was higher than ambient. Introduction of intercooling, which cools the intake air charge after the compressor and prior to the engine, helped to control piston temperatures. If piston temperatures were still too high, further cooling could be achieved by jets of oil onto piston under-crowns. Certain piston designs have an oil gallery within the piston crown to further aid the cooling process. Other piston design changes include reducing the clearances between the piston and liner to reduce lubricant consumption. Many of these changes have been used to reduce particulate emissions and allow higher peak cylinder pressures.

Piston problems occur when the lubricant forms an adherent carbonaceous coke as deposits in the piston grooves and lands, where lands are the areas adjacent to, and between, the piston grooves. Deposits in the grooves prevent the piston rings from seating correctly and may even immobilise them (ring sticking), resulting in cylinder compression loss and higher oil consumption. Deposits on the piston lands can wear away the bore honing marks to cause bore polish and lead to high oil consumption. Furthermore, piston deposit formation will lead to higher piston temperatures as the deposit provides thermal insulation. When this occurs, further deposit formation will accelerate and failure usually results. Most heavy-duty diesel oil specifications require piston deposits to be assessed. API specifications include cleanliness ratings for piston grooves, lands, piston skirts and under-crowns. European and Japanese specifications typically only require piston groove deposit ratings, e.g. in the Mercedes Benz OM441LA and the Nissan TD25. There are several different types of piston design used by heavy-duty diesel OEMs:

- cast iron piston,
- single-piece aluminium,
- two-piece design – aluminium skirt/steel crown,
- monometal design – single-piece steel.

Two-piece piston designs have been used in many heavy-duty diesel truck engines in North America. However, the API oil testing sequences only added a two-piece piston deposit test for API CH-4 in 1998. More recently some OEMs in North America have started using single-piece steel pistons. The piston deposit tests used within the API diesel oil specifications are listed in Table 9.8.

Table 9.8 API diesel deposit tests

API specification	Piston deposit test	Piston type	Fuel sulphur	Test
CF	Caterpillar 1M-PC	Single-piece Al	0.4% min	Single cylinder test
CF-4	Caterpillar 1K	Single-piece Al	0.4%	Single cylinder test
CG-4	Caterpillar 1N	Single-piece Al	0.05%	Single cylinder test
CH-4	Caterpillar 1P	Articulated steel crown/Al skirt	0.05%	Single cylinder test
CI-4	Caterpillar 1R	Articulated steel crown/Al skirt	0.05%	Single cylinder test
CJ-4	Caterpillar C-13	Articulated steel crown/Al skirt	15 ppm	In line six-cylinder engine test

European OEMs have used both two-piece steel crown/aluminium skirt and single-piece aluminium pistons to evaluate the piston deposit tendency of lubricants. The most common piston deposit test in Europe between 1994 and 2009 was the Mercedes Benz OM441LA engine dynamometer test. This engine uses a single-piece aluminium piston with a relatively high top land, i.e. the top piston groove is located well down the piston. The volume above the top groove, between liner and top piston land, is quite small in order to minimise particulate emissions. If poor quality lubricants are used, deposits can accumulate on the piston top land causing the liner to wear. The OM441LA engine test has tended to favour high ash and high detergent soap oils and lead to most top tier Mercedes lubricant formulations having high levels of detergent relative to the lower detergent API-only formulations.

The higher level of piston cleanliness, as measured for Mercedes Benz sheet 228.5 lubricants, has been correlated to long oil drain capability. Under certain conditions, lubricant service drains in excess of 100,000 km are possible for Mercedes

Benz heavy-duty diesel engines. Volvo and Scania, in contrast, have used field testing extensively to predict oil performance and extend oil drain intervals. In these field tests, many parts of the engine are rated, but piston cleanliness tends to be one of the most important rated parameters.

Fuel Quality: Diesel fuel quality can affect the performance of a diesel engine. The three main global specifications for on-highway diesel are ASTM D975 (US), EN 590 (EU) and JIS K2204 (Japan). ASTM D975 was introduced in 1993 and specified a sulphur limit of 500 ppm, superseding earlier requirements of 0.5%, with cetane number set at 40 minimum. The diesel fuel sulphur level can affect the performance of the lubricant, for at high diesel sulphur levels acids are produced in the combustion chamber. The acids from fuel combustion react rapidly with the overbased detergents in the lubricant. As the Base Number level in the lubricant drops it usually becomes necessary to change it, otherwise these acids will accumulate and degrade the lubricant and corrode the engine. This shows up as an increase in the Total Acid Number, TAN, of the lubricant. As TAN increases the bearings start to corrode, releasing lead into the lubricant. Furthermore, the iron wear rate will also rise dramatically at elevated TAN levels. One benefit of reduced sulphur diesel is that longer lubricant drain intervals are possible since less acid products are formed during fuel combustion. The converse is also true, with most OEMs recommending reduced oil drains intervals when high sulphur diesel is used.

Many modern trucks are equipped with after-treatment devices and to function properly, these will necessitate a further reduction in diesel fuel sulphur. To ensure compatibility with modern low-emission engines, i.e., US2007, Japan NLT (2005) and Euro IV (2004), fuel sulphur has been reduced to less than 10–15 ppm maximum.

US off-highway vehicles have used higher sulphur diesel compared to on-road, typically ~0.3% sulphur. From 2007, fuel sulphur requirements for off-highway vehicles were reduced to 500 ppm maximum. This fuel will be suitable for Tier 3 engines. Further cuts in fuel sulphur to 15 ppm maximum are scheduled for 2010 to enable Tier 4 to be met.

EN 590:1993 was the first EU diesel fuel specification, specifying a sulphur limit of 0.2% maximum with a cetane number at 49 minimum, somewhat higher than D975. A further update in 1999 as EN 590:1999, coincided with Euro 3 emission regulations and specified a maximum sulphur level of 350 ppm with a cetane number requirement increased to 51 minimum, overall referred to as ‘Euro 3 diesel’. For off-highway vehicles, the EN 590 directive introduces a 1000 ppm sulphur limit, effective from 2008.

Japan cetane numbers are typically set at 45 minimum, between the United States and Europe, with fuel sulphur levels progressively reduced from 0.2% maximum in 1994 to 50 ppm maximum in 2005. Like Europe, 10 ppm sulphur diesel was widely available from 2005 with a mandatory 10 ppm limit set in 2007.

As low-emission engine specifications are adopted globally, lower sulphur diesel is needed. Many countries in Asia Pacific are reducing diesel fuel sulphur, for example, China, India, Indonesia and Thailand all had diesel with less than 500 ppm sulphur by 2006. China, Korea, Taiwan and Australia also had some diesel at less than 50 ppm sulphur by the end of 2006. There are still many countries with diesel fuel sulphur in excess of 3000 ppm, causing lubricant drain intervals to be kept at relatively modest levels. High sulphur diesel hampers adoption of more modern low-emission diesel engine technology, especially those which requires the use of exhaust after-treatment.

Engine Lubricant Specifications: The American Petroleum Institute, API, approves the standards by which lubricant quality is assessed in North America. From 1985 onwards, there has been a plethora of lubricant specifications mainly associated with upgrades in engine technology to meet emission standards. Prior to 1985, the specifications were usually based on US military specifications MIL-L-2104.

The process approving lubricants is designated API 1509, 'Engine Oil Licensing and Certification System, 'EOLCS'. This is a voluntary system with the performance requirements and test methods set by ASTM and the OEMs, the latter being represented by the Engine Manufacturers Association, EMA. The performance level for heavy-duty diesel engine oils prior to 2007 is API CI-4 Plus, introduced in 2004 as a result of soot thickening issues in EGR-equipped trucks. This was an upgrade in API CI-4 performance, introduced in 2002. The API CI-4 category was developed without an EGR soot thickening test, and it was realised early on in the API CI-4 category that the existing non-EGR test, the Mack T-8E, was not adequate to predict soot-related viscosity increases in EGR-equipped engines. As a result, the Mack T-11 engine test using EGR was developed and adopted for API CI-4 Plus, and unlike the Mack T-8E engine test, requires the use of both conventional PIB-based dispersants and dispersant viscosity modifiers to disperse soot efficiently. The remaining tests for API CI-4 Plus cover all the other requirements including engine wear, piston deposits and engine cleanliness.

API CJ-4 includes several API CI-4 Plus tests together with additional tests on newer hardware. In addition, there are chemical limits required to ensure compatibility with after-treatment devices such as diesel particulate filters and diesel oxidation catalysts.

European engine lubricant specifications were established by CCMC until ACEA was formed in 1991. ACEA issued new lubricant specifications in 1996 and aimed to update them every 2 years. ACEA 2008 is the most recent heavy-duty diesel engine lubricant specification.

Japanese OEMs have historically recommended API CD combined with extra in-house requirements. The JASO M355:2000 DH-1 heavy-duty diesel lubricant category was released in 2001 to ensure a minimum quality level for all Japanese heavy-duty diesel engine lubricants. The quality level is similar to API CF-4 but with extra valvetrain wear and piston deposit requirements. Ash levels are typically greater than 1.4% with a minimum 10 TBN required, by ASTM D4739. JASO M355:2005 DH-2 was issued in 2005 to meet Japan's long-term emission regulations. The engine test requirements are the same as JASO DH-1 but with mandated chemical limits of $1.0 \pm 0.1\%$ sulphated ash to ensure compatibility with diesel particulate filters and after-treatment devices.

9.4 Motorcycles and Small Engines

9.4.1 Introduction

The lubricant requirements for motorcycles and small engines can be broadly split by their engine types: i.e. two-stroke or four-stroke. Small engines cover lightweight portable equipment such as chainsaws through to applications such as personal watercraft or snowmobiles.

9.4.2 Overview of Two-Stroke Lubricants

Historically, the two-stroke engine has been a dominant force in the world of motorcycling and portable equipment due to its high power-to-weight ratio, simplicity of construction and low cost compared to equivalent sized four-stroke engines.

By their design, two-stroke engines have different lubrication requirements from four-stroke automobile engines. Two-strokes rely on 'lost oil' lubrication where a continuous feed of lubricant into the engine is burned or 'lost' and replenished every cycle. This lubricant may be either pre-mixed with the fuel or injected via a small metering delivery pump into the engine as a function of throttle position. Two-stroke lubricants must have a number of important attributes, mainly:

- keep pistons and rings free from deposits,
- prevent spark plug fouling/whiskering,
- prevent exhaust port and silencer blocking,
- prevent scuffing of the piston/cylinder assembly,
- reduce visible exhaust smoke,
- prevent crankcase deposit formation,
- reduce the risk of detonation/pre-ignition.

9.4.3 Two-Stroke Specifications

There are a number of different two-stroke lubricant standards available in the industry from API, TISI (Thai Industrial Standards Institute), CEC and JASO with JASO M345 being, perhaps, the most dominant and comprehensive standard. The JASO system, Table 9.9, ranks lubricants by their performance features/benefits relative to high- (JATRE 1) and low-reference (JATRE 3) lubricants. The higher the index for each parameter in Table 9.9 the better the performance of the lubricant, with the high reference position giving an index of 100 in each test. The parameters scored are:

- smoke (visible exhaust smoke),
- detergency (piston cleanliness and ring sticking),
- exhaust system blocking (exhaust restriction leading to power loss),
- lubricity (piston seizure resistance).

Table 9.9 JASO M345 indices by performance area

		Lowest level		Highest level	
Area of interest	Index	JASO FA*	JASO FB	JASO FC	JASO FD
Smoke	'SIX'	40	45	85	85
Blocking	'BIX'	30	45	90	90
Lubricity	'LIX'	90	95	95	95
Detergency	'DIX'	80	85	95	>125**
		Lowest performance		Highest performance	

*Obsolete; **3 h test (Reprinted with the permission of J-SAE)

Lubricant Composition: In terms of composition, two-stroke lubricants comprise a number of key constituents, Table 9.10, with each component playing a specific role depending on the specification and performance requirements of the OEM or lubricant marketer, Table 9.11.

Table 9.10 Two-stroke lubricants' key constituents

Component	% Weight in formulation	Function
Performance additives	Up to 6%	Engine cleanliness
Bright stock	Up to 10%	Lubricity, antiwear
Solvent	10–30%	Miscibility, pumpability, exhaust blocking
Polyisobutene (PIB)	10–30%	Clean burning for low smoke performance
Base oil	Up to 95%	Lubricity, antiwear, carrier fluid

Table 9.11 Typical two-stroke composition make-up, depending on specification

	JASO FA	JASO FB	JASO FC	JASO FD
Performance additives	*	**	***	****
Bright stock	**	*	–	–
Solvent	–	*	***	***
PIB	–	–	***	***
Base oil	***	**	*	*

The symbol represents relative concentration of the different components

Performance Additives: Two-stroke lubricants do not contain conventional antiwear chemistry such as ZDDP, the main reason being the lack of highly loaded surfaces such as cams in the engine. Instead, viscosity alone is the main antiwear component in two-stroke oils, which is driven predominantly by the choice of base oil in the formulation. For the short time that the lubricant is in the engine, it must have sufficient inherent viscosity to prevent the piston assembly from scuffing against the liner. For this reason, JASO recommends that two-stroke engine lubricant viscosities should always be above 6.5 cSt at 100°C.

Because lubricant is burnt in every combustion cycle, two-stroke engines are highly sensitive to ash levels. Lubricants containing high ash levels such as four-stroke motor lubricants can lead to the rapid build-up of spark plug, cylinder head and piston crown deposits resulting in pre-ignition or detonation – and a rapid failure of the piston or spark plug, Table 9.12.

Table 9.12 Ash comparison by application

Application	Outboard 2-T	2-T Motorcycle	4-T Motorcycle	4-T Car	4-T Truck
Typical % ash	'Ashless'	<0.25	<1.2	<1.2	<2.0

The choice and level of detergents and dispersants used in two-stroke formulations and their contribution to ash is therefore critical to prevent in-service failure due to pre-ignition. This is particularly important in cool running, highly stressed outboard applications, where low ash or 'ashless' systems are commonly used.

Solvents: The primary purpose of the solvent in a two-stroke system is to assist with the miscibility of the finished oil with the fuel and also to aid pumpability in auto-lube systems. Whilst kerosene is often used, de-aromatised solvents are more commonly used with flash points of around 80°C.

PIB: When mineral base oil is substituted by PIB in two-stroke formulations, it burns cleanly or 'un-zips' chemically which has a significant effect on visible smoke emissions. Various types of PIB can be used, but the PIBs typically used in conventional low smoke oils have molecular weights in the range 450–1250 Mw. These may be either straight cut or dumb-bell systems. Very high molecular weight PIB can cause issues with detergency and startability (due to the increased tackiness of the oil), whilst very low molecular weight systems may lack lubricity.

Base Oils: In most cases, standard quality two-stroke oils will use mineral base oils such as bright stock (to provide lubricity) and a medium cut such as 500 N. Synthetic base oils, including esters, may be used in high-performance two-stroke engine oils, where exceptional film strength is required to prevent seizure under high load, high temperature conditions. Examples would include chainsaw engine lubricants and two-stroke racing lubricants.

In more environmentally sensitive areas such as boating, snowmobiles and to some extent with chainsaws, the need for readily biodegradable two-stroke lubricants has arisen leading to a number of biodegradable products in the marketplace using complex ester-based technology.

Emissions and the Future: One of the main drawbacks of the two-stroke engine is high hydrocarbon and CO emissions, resulting from a number of factors:

(i) oil is being burned with the fuel,
(ii) hydrocarbons from the oil can pass straight into the exhaust,

(iii) unburned fuel can pass straight through the exhaust due to ‘short circuiting’ of the inlet and exhaust ports,
(iv) high oiling rates in pre-mix systems, up to 3% lubricant in fuel,
(v) pooling of lubricant in the crankcase during idle conditions, giving high smoke levels during acceleration.

On the positive side, two-stroke engines have generally low NO_x emissions as a result of the natural exhaust gas recirculation (EGR) effect of the port scavenged design, where a portion of the exhaust gas is drawn back into the crankcase during each induction cycle.

There have been a number of technological advances which have improved the viability of the two-stroke from an emissions standpoint which include:

(i) introduction of low smoke lubricants (JASO FC and above),
(ii) introduction of ‘auto-lube’ systems, giving minimal oiling at low speed to prevent over-oiling at idle,
(iii) introduction of fuel injection systems, enabling fuel to be injected into the cylinder once the transfer ports have closed on the compression stroke to negate short circuiting in the crankcase,
(iv) introduction of oxidation catalysts in 2T applications.

Whilst steps can be made to improve the two-stroke from an emission’s standpoint, the four-stroke engine has become the dominant power unit for today’s motorcycles. Two-strokes continue to be used in off-road/racing applications, small, <50 cc, scooters, boating and portable equipment.

9.4.4 Four-Stroke Motorcycle Lubricants – Overview

The similarities between passenger car engine lubricants and those of four-stroke motorcycles are, in themselves, obvious enough. There are, however, a number of key engineering design features of motorcycles which place additional stress/requirements on the lubricants they use:

- high speed of operation (up to 16,000 rpm),
- high specific power output (up to 150 kW/l),
- low sump volumes,
- integral wet clutch and gearbox, common on many modern engines, lubricated by the engine lubricant,
- lightweight engine construction.

9.4.5 Four-Stroke Motorcycle Specifications

Up until the mid-1990s, there was no specific standard for four-stroke motorcycle engine lubricants with the API gasoline specification being the most widely used. The trend towards fuel efficient passenger car lubricants, through low viscosity and friction modification and its impact on motorcycle performance led to the development of JASO T903 – a dedicated four-stroke motorcycle specification which was updated in 2006. The standard addresses a number of motorcycle specific issues beyond standard gasoline specifications – mainly gasoline engine lubricant technology, plus:

- wet clutch performance,
- gearbox protection,
- physical/chemical constraints.

Wet clutch performance is measured by assessing the lubricant's frictional behaviour relative to high-friction (JAFRE A) and low-friction (JAFRE B) reference oils in JASO T904-98, as a modified SAE#2 friction test for motorcycle applications. The test evaluates three main clutch parameters:

- static friction, relating to clutch slip,
- dynamic friction, relating to clutch feel/take up,
- stop time, relating to synchronisation time.

A clutch performance index is then assigned to the oil, which can then be classified according to Table 9.13 as JASO MA, MA1 and MA2 (high friction, suitable for wet clutch applications) or JASO MB (low friction, more suited to dry clutch or scooter applications).

Table 9.13 JASO T903 clutch friction specifications

		JASO T 903 2006 indices			
		High friction			Low friction
Parameter	INDEX	JASO MA	JASO MA2	JASO MA1	JASO MB
Dynamic friction index	DFI	$1.45 \leq SFI < 2.5$	$1.8 \leq SFI < 2.5$	$1.45 \leq SFI < 1.8$	$0.5 \leq SFI < 1.45$
Static friction index	SFI	$1.15 \leq SFI < 2.5$	$1.7 \leq SFI < 2.5$	$1.15 \leq SFI < 1.7$	$0.5 \leq SFI < 1.15$
Stop time index	STI	$1.55 \leq SFI < 2.5$	$1.9 \leq SFI < 2.5$	$1.55 \leq SFI < 1.9$	$0.5 \leq SFI < 1.55$

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For a lubricant marketer to claim JASO MA1 or JASO MA2, all indices must fall within the values specified for the category. If the frictional indices are shared between JASO MA1 and JASO MA2, then the oil must claim JASO MA. The lubricant marketer also has the choice to claim JASO MA on lubricants meeting JASO MA1 or JASO MA2. To claim JASO MB, at least one or more of the indices must meet the criteria for JASO MB in Table 9.14.

As the integral motorcycle gearbox design can often give rise to higher shear loss in multi-grade lubricants than when used in a passenger car application, after-shear targets are set which reflect this whilst retaining sufficient base viscosity to afford an acceptable degree of gearbox wear protection from pitting or scuffing, Table 9.14.

Table 9.14 Comparison of J300 and T903 shear loss requirements for multi-grade oils

	After-shear kinematic viscosity at 100°C (30 cycle, ASTM 6278)			
Viscosity grade	Other grades	xW-30	xW-40	xW-50
SAE J300	Stay in grade	≥9.3	≥12.5	≥16.3
JASO T903	Stay in grade	≥9.0	≥12.0	≥15.0

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A number of additional physical/chemical constraints are present in the specification, including:

- a minimum API service quality level of API SG,
- a minimum ‘High Temperature High Shear, HTHS’, viscosity of 2.9 cP for bearing protection,
- a maximum ash level of 1.2%,
- a maximum phosphorus level of 0.12% to provide catalyst durability,
- a minimum phosphorus level of 0.08% to give assured gearbox protection in light of modern low phosphorus passenger car engine oils.

9.4.6 Lubricant Composition and Impact on Clutch Performance

In general, four-stroke motorcycle engine lubricants use the same additive components as passenger car engine lubricants. The exact choice and levels differ in the four-stroke motorcycle lubricant to cater for increased high-temperature performance and, more importantly, to ensure proper operation of the wet clutch system which is both lubricated and cooled by the engine oil. Each component in the finished oil may influence the clutch performance. A typical response to clutch performance of these components is presented in Table 9.15. No system is unique, however, with differing clutch friction materials, oil feed rates and clutch spring rates also influencing the performance of any single clutch system.

Table 9.15 Typical formulation impact on SAE#2 clutch friction

<table>
<tr><th></th><th colspan="3">Impact on wet clutch performance</th></tr>
<tr><th>Constituent</th><th>Negative</th><th>Neutral</th><th>Positive</th></tr>
<tr><td>Detergent</td><td></td><td colspan="2">Type specific</td></tr>
<tr><td>Dispersant</td><td></td><td>Type specific</td><td></td></tr>
<tr><td>ZDDP</td><td></td><td>Type specific</td><td></td></tr>
<tr><td>Friction modifier</td><td>*</td><td></td><td></td></tr>
<tr><td>Antioxidant</td><td colspan="2">Type specific</td><td></td></tr>
<tr><td>Viscosity modifier</td><td>Dispersant VMs</td><td>OCP Type</td><td></td></tr>
<tr><td>Mineral base oils</td><td></td><td>*</td><td></td></tr>
<tr><td>Synthetic base oils</td><td></td><td>Type/viscosity specific</td><td></td></tr>
<tr><td>Antifoam</td><td></td><td>*</td><td></td></tr>
<tr><td>PPDs</td><td></td><td>*</td><td></td></tr>
<tr><td>Dye</td><td></td><td>*</td><td></td></tr>
</table>

9.4.7 Emissions and the Future

The advances seen in gasoline engines such as fuel injection, multi-valve technology and three-way catalysts are becoming more mainstream in higher performance motorbikes as they strive to meet increasingly stringent emission targets.

Fuel economy, particularly in emerging markets, is also a primary driver for change with lower viscosity lubricants, 10W30, becoming more accepted in the marketplace in modern engines. Additionally, the trend towards longer drain intervals for motorcycles will place additional stress on the lubricant – especially in machines having sump volumes as low as 0.7 l which operate in high-temperature environments.

Although automotive gasoline engine oil specifications will continue to influence four-stroke motorcycle engine lubricant specifications, critical differences in motorcycle engine design and lubricant appetite will demand the need for motorcycle-specific lubricant tests to ensure protection and performance in this highly stressed application.

Chapter 10
Driveline Fundamentals and Lubrication

I. Joseph

Abstract The various gear types and automotive transmissions in drive trains are described. The need for automotive differential axle gears is demonstrated. SAE gear lubricant classifications are related to performance specifications. Automatic transmission fluids, ATFs, are described together with agricultural and off-highway fluids. Generic formulations of driveline fluids are discussed in terms of their tribology and performance and also the contribution of various additive classes to that performance. The main functions of manual gearbox, automatic transmission and axle lubricants are described. General trends and emerging technologies in drive train components are discussed in terms of the requirements placed on the lubricant, evolution in transmission technologies and relative market penetration.

10.1 Introduction to Transmission Systems

The first known transmission appeared in 1832 when English coach-maker W. H. James introduced a variable-ratio transmission which allowed an impressive three speeds. Frenchmen Rene Panhard and Emile Levassor were later credited with inventing the modern transmission when they installed a clutch-mounted gearbox in their 1895 Panhard model. In 1908, Leonard Dyer obtained one of the first patents for an automobile transmission. The earliest passenger cars were equipped with manual transmissions, but as technology progressed and vehicle size and traffic increased, the need for an automatic transmission arose. Shortly before World War II, the first automatic transmission appeared on an Oldsmobile after development of the ‘Hydra-matic Drive’ by General Motors. Shortly after, Chrysler produced its own automatic transmission system, and by 1948, all major US carmakers proposed models with optional automatic transmissions. The creation of the automatic transmission has marked the most important evolution in this sector. Further improvements met a variety of needs and adapted to new technical requirements such as transverse engines and all-wheel drive, AWD, and to achieve improved operating performance. The underlying technology, however, remained virtually the same.

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DOI 10.1023/b105569_10,

10.2 Gear Types

Gears are mechanical devices that transfer rotating motion and power from one part of a machine to another. In transmissions, gears are used for increasing and decreasing torque, changing speed and/or changing direction of movement. When two gears mesh or run together, the larger gear is called the ring gear and the smaller gear the pinion gear. Different kinds of gears and gear arrangements are used to perform different functions, Fig. 10.1.

Spur gears are the simplest gear, of three types: external, internal and rack and pinion. All have straight teeth cut parallel to the axis. Because only one set of teeth is in contact at any one time, the load-carrying capacity of these gears is limited.

Helical gears are a modification of spur gears where the teeth are cut at an angle to the axis, allowing more than two teeth to be in contact at a time. This increases their load-carrying capacity, and they find extensive use in high-speed transmissions. A double helical gear, commonly known as herring bone gear, has two opposed helices which further increases the load-carrying capacity.

Bevel gears are cut to produce teeth as truncated cones. A s*imple bevel* gear has straight teeth radiating from the points of the cone. A s*piral bevel* gear has curved teeth at an angle to radial lines. These structural modifications increase the area of contact and hence the load-carrying ability. Spiral bevel gears can carry a greater load than straight bevel gears and are quieter in operation at all speeds.

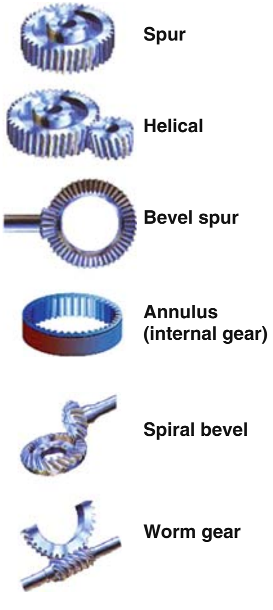


Fig. 10.1 Different types of gears

Worm gears are used where shafts are at right angles and have maximum offset. The long gear is the worm, and the round gear is the wheel gear. These gears experience maximum sliding and extensive contact.

Hypoid gears have both the characteristics of the spiral bevel gears and worm gears, with the axle offset. Their design provides very high load-carrying capacity and quieter operation. Hypoid gears are used mostly for automotive applications, and the axle offset permits the lowering of the driveshaft. Because of the increased areas of contact due to sliding, these gears can be difficult to lubricate.

Lubrication requirements for different types of gears are related to their load-carrying capacity which, in turn, depends upon the area of contact and the amount of slide relative to roll during motion. The higher the area of contact, the higher the load-carrying capacity and higher the slide-to-roll ratio, the more demanding the lubrication requirements. Spur gears, with the lowest load-carrying capacity, are at one extreme, and the offset hypoid gears, with the highest load-carrying capacity, are at the other extreme with respect to lubrication requirements.

10.3 Transmissions

10.3.1 Manual Transmissions

To understand the basic idea of a standard manual transmission, Fig. 10.2 shows a very simple two-speed transmission in neutral:

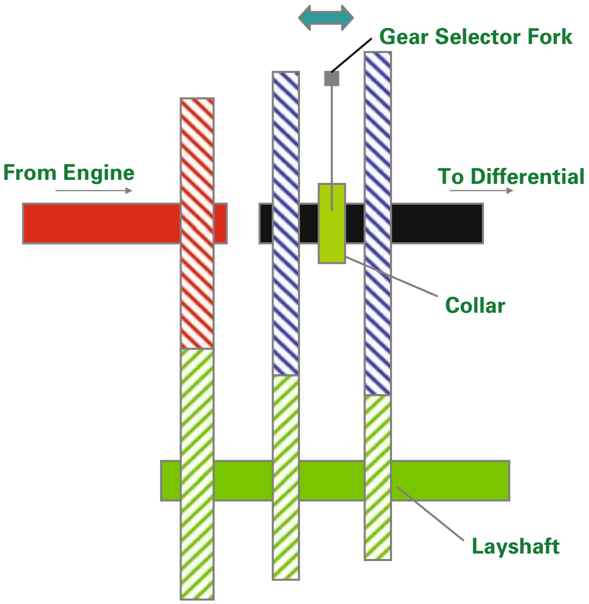


Fig. 10.2 A simple two-speed manual transmission

- The red shaft is connected to the engine through the clutch. The clutch is a device to connect and disconnect the engine and the transmission. When the clutch pedal is pushed in, the engine and the transmission are disconnected so the engine can run even if the car is standing still. When the clutch pedal is released, the engine and the red shaft are directly connected to one another. The red shaft and gear are connected as a single unit and turn at the same speed as the engine.
- The green shaft and gears are called the layshaft. These are also connected as a single piece, so all of the gears on the layshaft and the layshaft itself spin as one unit. The red shaft and the green shaft are directly connected through their meshed gears so that if the red shaft is spinning, so is the green shaft. In this way, the layshaft receives its power directly from the engine whenever the clutch is engaged.
- The black shaft is a splined shaft that connects directly to the driveshaft through the differential to the drive wheels of the car. If the wheels are spinning, the black shaft is spinning.
- The blue gears are on bearings, so they spin on the black shaft. If the engine is off but the car is coasting, the black shaft can turn inside the blue gears while the red gears and the layshaft are motionless.
- The purpose of the collar is to connect one of the two blue gears to the black driveshaft. The collar is connected, through the splines, directly to the black shaft and spins with the black shaft. However, the collar can slide left or right along the black shaft to engage either of the dark blue gears. Teeth on the collar, called dog teeth, fit into holes on the sides of the blue gears to engage them.

10.3.2 Synchromesh Systems

Synchromesh systems use friction to match or synchronize gear speeds before shifting gear. Using a synchromesh gearbox means that the driver does not have to think about engine speed and vehicle speed when changing gear, therefore there is no gear 'crashing' and no need for 'double clutching'. The main components of a typical synchromesh system are shown in Fig. 10.3.

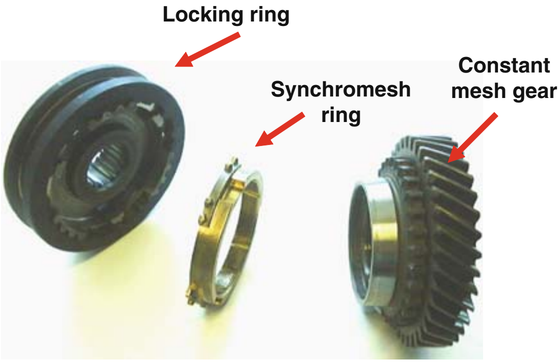


Fig. 10.3 Synchromesh system components

10.3.3 Automatic Transmissions

Just as for a manual transmission, the automatic transmission's primary job is to allow the engine to operate over a relatively narrow range of speeds whilst providing a wide range of output speeds. Also, as with vehicles with manual transmissions, vehicles with automatic transmissions need to let the engine turn whilst the wheels and gears in the transmission have stopped. As described in Section 10.1, manual transmissions use a clutch to completely disconnect the engine from the transmission. Automatic transmission cars use a torque converter situated between the engine and the transmission which is a fluid coupling which allows the engine to spin somewhat independently of the transmission, to the left in Fig. 10.4. If the engine is turning slowly, such as when the car is idling at a stop, the torque passed through the torque converter is very small, and keeping the vehicle still only requires light brake pressure. If the engine accelerates whilst the vehicle is stopped, harder brake pressure is required to keep the vehicle from moving. This is because when the engine accelerates and pumps more fluid into the torque converter, more torque is transmitted to the wheels.

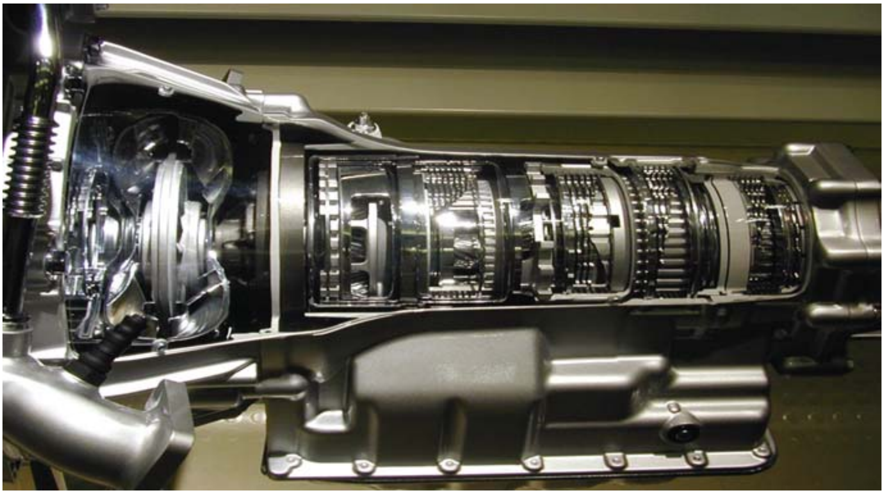


Fig. 10.4 Cutaway view of an automatic transmission

The key difference between a manual and an automatic transmission is that the manual transmission locks and unlocks different sets of gears to the output shaft to achieve the various gear ratios. In an automatic transmission, the same set of gears produces all of the different gear ratios through a planetary gearset.

Planetary Gearsets: An automatic transmission has a very large number of parts in a relatively small space, Fig. 10.4, assembled into subsystems, the major ones being:

- a planetary gearset,
- a set of bands to lock parts of the gearset,
- a set of three wet-plate clutches to lock other parts of the gearset,
- a complex hydraulic system that controls the clutches and bands,
- a large gear pump to transfer transmission fluid and give hydraulic pressure to operate the clutches.

The centre of an automatic transmission is the planetary gearset which creates all of the different gear ratios that the transmission can produce. All of the other components in the transmission are present to enable the planetary gearset to operate efficiently. An automatic transmission contains two complete planetary gearsets folded together into one component, Fig. 10.5. By locking different component gears of the planetary gearset at constant input shaft speeds, different output shaft speeds are generated.

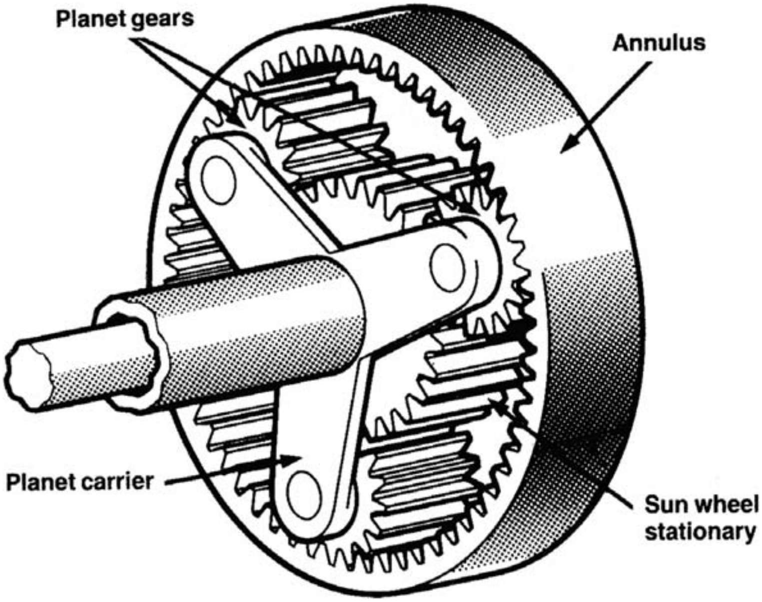


Fig. 10.5 Planetary gearsets as in an automotive automatic transmission

10.3.4 Axles and Differentials

Most axles are combined with a differential, Fig. 10.6, and have three main functions:

- to transfer the engine power to the wheels,
- to be the final gear reduction in the vehicle, reducing the rotational shaft speed from the gearbox to the road wheel speed,

- to transmit the power to the wheels whilst allowing them to rotate at slightly different speeds – this function is the one that earned the differential mechanism its name.

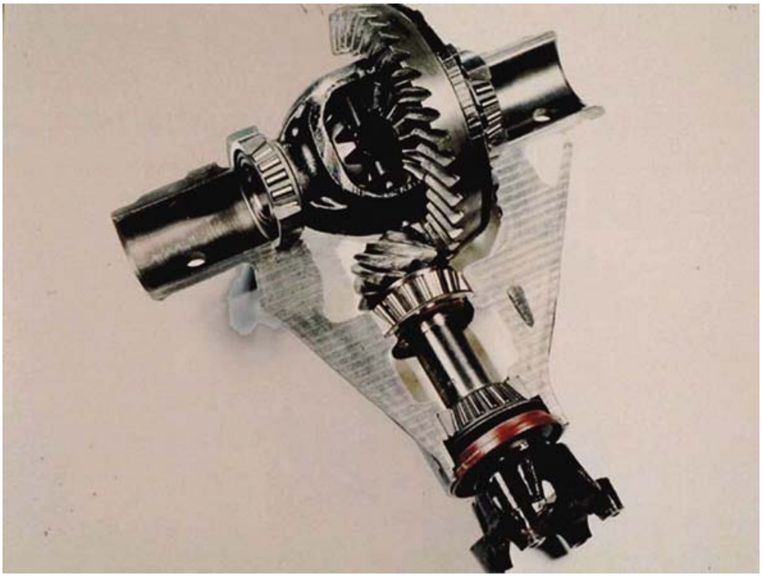


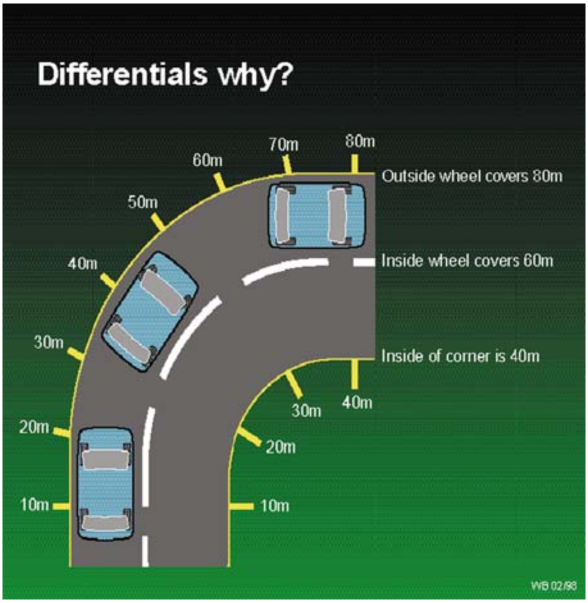
Fig. 10.6 A rear axle drive combined with a differential

Figure 10.6 shows the shaft, bearing and gears which would be within a typical axle housing. The offset spiral bevel gears turn the line of rotation through 90°, and the differential mechanism is contained within the housing at the centre of the large gear. The need for a differential is shown in Fig. 10.7, explaining the different distances travelled by the inner and outer wheels on the same driven axle when a vehicle traverses a bend in a road. When a vehicle drives round a corner, the outer wheel travels further than the inner, and:

- to do this, they need to travel at different speeds,
- for the non-driven wheels on a vehicle, this is not an issue as there is no connection between them, so they move independently,
- the driven wheels are linked together so that a single engine and transmission can turn both wheels. Without a differential, the wheels would be locked together and forced to travel at the same speed, which would make turning difficult, hard on the vehicle and particularly the tyres, as one of the two must slip.

Whilst both necessary and effective, the unintended problem with standard differentials is when one of the wheels slips, such as in mud, on a wet road or on ice. All of the engine power is delivered to the slipping wheel and none to the other

Fig. 10.7 Explanation of why a differential is needed



wheel which has adhesion and is stationary. The vehicle is stuck under these conditions. The solution to this is a limited slip differential, Fig. 10.8, which prevents all power being transferred to one wheel when that wheel is on a slippery surface, e.g. ice or mud, as described.

In the limited slip differential, clutches apply friction to the shaft of the spinning road wheel. This diverts rotational power to the opposite shaft, allowing the vehicle to gain traction and move off on the slippery surface.

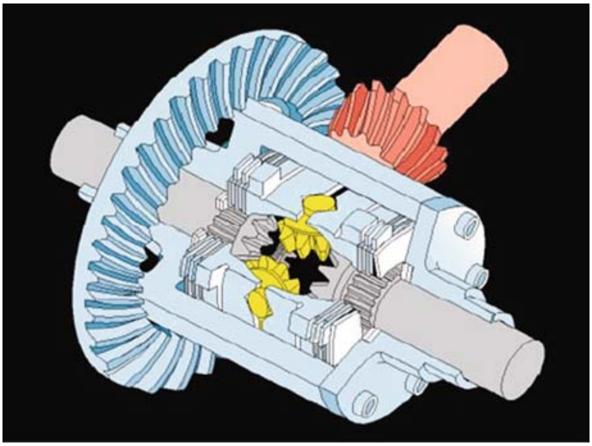


Fig. 10.8 A limited slip differential

10.4 Industry Specifications for Gear Oils

10.4.1 Introduction

Automotive gear oils are classified in a manner similar to that of engine lubricants, i.e. through SAE viscosity grades, API service designations, US Military Specifications and OEM performance requirements. However, it is important to note that SAE viscosity grades for gear lubricants are different to those of engine lubricants. The SAE grade numbers for one application are independent of those for the other. For example, the viscosity range for a SAE 75W grade in gear lubricants is not as significantly higher than that for SAE 10W grade in engine oils as the higher numerical rating may suggest. Similarly, the viscosity characteristics of an SAE 90 grade gear oil is similar to those of an SAE 50 grade engine oil. SAE J306 is an international standard defining automotive gear lubricant viscosity grades analogous to SAE J300 for engine lubricants. Monograde lubricants meet a single viscosity grade, whilst products meeting more than one specification are designated as multigrades. Until May 2005, there were only nine viscosity classifications, but OEMs felt that the higher viscosity grades, SAE 90 to SAE 250, were too broad. A lubricant could be used that met OEM viscosity grade requirements but be significantly higher or lower than originally validated for use. A unanimous ballot was passed in April 2005 to introduce two new viscosity grades, between 90 and 140 and also between 140 and 250, highlighted red in Table 10.1.

Table 10.1 SAE 306 gear lubricant classifications

J306	KV 100°C cSt Min.	KV 100°C cSt Max.	Brookfield viscosity: max 150,000 cP @ Temp., °C	Min. KV 100°C After 20 h KRL
70W	4.1	–	–55	4.1
75W	4.1	–	–40	4.1
80W	7.0	–	–26	7.0
85W	11.0	–	–12	11.0
80	7.0	11.0	–	7.0
85	11.0	13.5	–	11.0
90	13.5	18.5	–	13.5
110	18.5	24.0		18.5
140	24.0	32.5	–	24.0
190	32.5	41.0		32.5
250	41.0	–	–	41.0

Numerous performance specifications can be used to identify the level of protection given by an automotive gear lubricant. In the past, API Category GL-4 was commonly used to describe the type of lubricants that would provide acceptable performance in manual transmissions and lightly loaded final drive axles. API Category GL-5 described lubricants that were generally used in final drive axles operating in moderate to severe service. However, several new performance specifications are becoming the benchmark for describing lubricant quality.

API Category MT-1, issued in 1995, describes the performance requirements of lubricants intended for use in non-synchronized manual transmissions, such as those found in heavy-duty trucks and buses, particularly in the United States. Lubricants meeting this requirement give protection against the combination of thermal degradation, component wear and oil seal deterioration which is not provided by lubricants meeting the requirements of API GL-1 through to GL-5.

MIL-PRF-2105E, also released in 1995, combines the performance requirements of its predecessor, MIL-L-2105D and API MT-1. Whilst MIL-PRF-2105E and its predecessors have been widely recognized and used in many areas of the world, it has not been adopted globally, primarily because lubricant blenders and marketers in non-NATO countries have not been able to obtain a formal approval under this specification.

SAE J2360: The US Department of Defense published a Directive in 1991 to adopt non-governmental standards in preference to federal and military specifications whenever practical. This relieved government of the burden of maintaining these specifications, and one outcome was that SAE rewrote MIL-PRF-2105E as SAE J2360. Being identical, the added benefit was that a lubricant supplier anywhere in the world can obtain formal approval and have their name, and that of their approved product, published on a Qualified Product list. In turn, this means that equipment manufacturers now have a means to specify and identify high-quality lubricants for use in their equipment anywhere in the world.

10.4.2 API Service Designations in Current Use

API GL-1. Lubricants intended for manual transmissions operating under such mild conditions that straight petroleum or refined petroleum oil may be used satisfactorily. Oxidation and rust inhibitors, defoamers and pour point depressants may be used to improve the characteristics of these lubricants. Friction modifiers and extreme pressure additives may not be used.

API GL-4. Lubricants intended for axles with spiral bevel gears operating under moderate to severe conditions of speed and load or axles with hypoid gears operating under moderate speeds and loads. These oils may be used in selected manual transmissions and transaxle applications, where API MT-1 lubricants are unsuitable.

API GL-5. Lubricants intended particularly for hypoid gears in axles operating under various combinations of high-speed shock loads and low-speed, high-torque conditions. Lubricants qualified under MIL-L-2105D, E or SAE J2360 satisfy the requirements of the API GL-5 specification, although the API designation does not require military approval.

API MT-1. As described above. Note that it does not address the performance requirements of synchronized transmissions and transaxles in passenger car and heavy-duty applications.

10.4.3 API Service Designations NOT in Current Use

API GL-2 Lubricants intended for automotive worm gear axles operating under such conditions of load, temperature and sliding velocity that lubricants satisfying API GL-1 service will not suffice. Products suited for this type of service contain anti-wear additives or film-strength improvers specifically designed to protect worm gears.

API GL-3 Lubricants intended for manual transmissions operating under moderate to sever conditions and spiral bevel axles operating under mild to moderate conditions of speed and load. These service conditions require lubricants having good load-carrying capacities exceeding those satisfying API GL-1 but below those satisfying API GL-4. API GL-3 service lubricants are not intended for axles with hypoid gears.

API GL-6 Lubricants intended for gears designed with very high pinion offsets. Such designs typically require protection from gear scoring in excess of that provided by GL-5 gear oils. A shift to more modest pinion offsets and the obsolescence of original API GL-6 test equipment and procedures have greatly reduced the commercial use of these lubricants.

10.5 Automatic Transmission Fluids, ATFs

In general, ATF performance is defined by the service-fill specifications of passenger car and commercial vehicle transmission manufacturers. These specifications establish both testing procedures and the pass/fail criteria for the performance parameters.

Historically, two major passenger car manufacturers in the United States, GM and Ford, have led the automatic transmission fluid industry specification with their Dexron® and Mercon® ATF service-fill specifications, respectively. However, in recent years, most automatic transmission manufacturers and vehicle OEMs have moved to extended drain, heavy-duty or fill for life (FFL) performance from their automatic transmission fluids. The consequence is that each automotive transmission manufacturer/OEM has a much more focused approach on optimizing the fluid for their automatic transmission and no longer finds the GM or Ford specifications acceptable as standards. At the time of writing, globally there are at least 13 different automatic transmission fluid specifications covering passenger car factory-fill and service-fill requirements. It is not the intention of this chapter to go through this complex scenario in any detail.

10.6 Agricultural and Off-Highway Fluids

The agricultural fluids’ market can be split into two broad groups:

- STOU, Super Tractor Oil Universal,
- UTTO, Universal Tractor Transmission Oil.

The difference between the two groups is that an STOU can be used to lubricate the transmission, hydraulics and wet brake system as well as the engine on a tractor, whereas the UTTO can be used for the same applications *except* in the engine.

STOUs found widespread use in the late 1980s and 1990s because of their versatility. But heavy-duty diesel engine oil specifications evolved, and the technical challenge of meeting all the driveline needs and the more demanding engine oil requirements in one product was too great. STOUs remained with their engine credentials not evolving to meet the demands of the modern engines. STOUs still find widespread use in older tractors, but the belief is that this type of lubricant will be gradually phased out of the market.

UTTOs are specifically formulated for driveline performance, including transmissions, final drives, wet brakes and clutches and also hydraulic systems, typically from a common sump on the tractor. This unique combination of performance characteristics makes tractor fluids acceptable for use in both on and off-highway commercial transmissions and high-pressure hydraulic systems. They can also be used in mining equipment. Tractor Fluid specifications are dominated by four manufacturers:

- John Deere, J20C/D, J27,
- Ford NH, 134D,
- Massey Ferguson, now part of AGCO, M1135, M1143, M1144 and M1145,
- Case NH, MS 1207, MS1210.

Each specification is specific to each OEM, but it is possible to have one product that meets more than one specification. The specifications for these fluids in general deal with extreme pressure, EP, and antiwear properties and also with matching the frictional requirements of the equipment. The quality of these fluids is assessed on the basis of their ability to meet individual OEM specifications as well as API GL-4, for EP, Allison C-4, for friction, oxidation, and wear, and Caterpillar TO-4, for friction, performance requirements.

10.7 Generic Formulation of Driveline Fluids

10.7.1 Introduction

One of the most important properties of driveline fluids is their frictional performance in terms of both the level and durability. The fluid also has to be compatible with the components inside the transmission. Optimizing the frictional characteristics of a fluid for a particular application is absolutely critical to ensure trouble-free operation of the equipment, whether it be an automatic gearbox, synchronized manual gearbox or the wet brake system in a tractor. The problems that can be encountered are:

– dynamic friction too high → gear change time very short and uncomfortable,
– dynamic friction too low → gear change time too long, feeling of clutch slipping,

– friction rising as slip speed reduces → clutch plates lock suddenly, causing judder/shudder/jerking of the machine, Fig. 10.10,
– static friction too low → clutch slips even when fully engaged, poor torque transmission.

The 'ideal' friction curve shape that is desired is the same almost irrespective of the application: that is a decreasing dynamic friction coefficient with reducing speed, i.e. as the clutch is closing or locking up, Fig. 10.9. Also the static friction coefficient, μ_s, must be less than the dynamic friction coefficient, μ_d, i.e. $\mu_{s/}\mu_d < 1.0$. Satisfying these two criteria will generally ensure smooth engagement of the moving parts. Having achieved the ideal friction curve, it is also desirable to maintain those frictional characteristics throughout the lifetime of the transmission. The factors that affect this important parameter are:

- test conditions, i.e. speed, load and temperature,
- materials, i.e. clutch friction material and the metallurgy of the steel reaction plate,
- the lubricant.

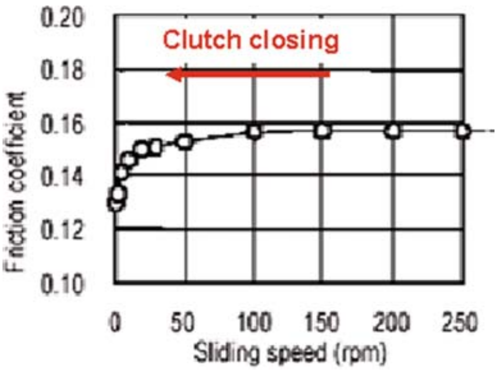


Fig. 10.9 Good frictional performance when clutch closes, $\mu_s < \mu_d$

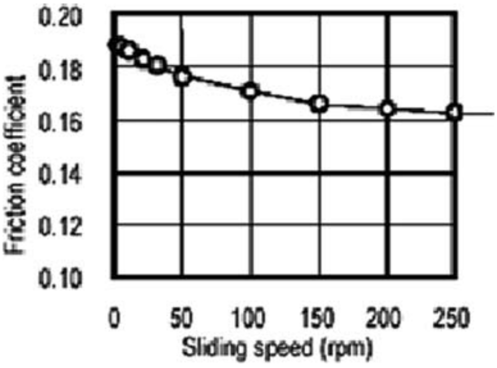


Fig. 10.10 Poor frictional performance when clutch closes, $\mu_s > \mu_d$

10.7.2 Automatic Transmission Fluids

The most complex driveline fluid is the automatic transmission fluid; a typical fluid has to provide the following performance characteristics:

- transmit power,
- act as a hydraulic fluid,
- remove heat efficiently,
- provide the correct frictional response,
- protect gears and bushings,
- operate at temperature extremes,
- non-corrosive to all transmission components,
- special antifoam properties,
- seal compatibility.

The additive pack used to formulate an automatic transmission fluid can contain up to 20 different additive components, as summarized in Table 10.2.

Table 10.2 Typical components of an automatic transmission fluid

Additives	Treat rates	Functions
Dispersants 2 or 3	2–6%	Cleanliness, disperse sludge, friction and wear
Detergents 1 or 2	0.1–1.0%	Cleanliness, friction, corrosion inhibition and wear
Anti-oxidants 1 or 2	0.3–1.0%	Control oil thickening, prevent varnish and deposits
Antiwear 1	0.1–0.5%	Protection of epicyclic gears
Friction modifiers 2 or 3	0.2–1.5%	Control shift feel and friction durability of clutches
Corrosion inhibitor 1	0.03–0.5%	Prevent corrosion, rust, pitting and wear
Antifoam 1 or 2	50–400 ppm	Prevent excessive foaming and air entrainment
Seal swell agent	0.3–1.5%	Combats seal embrittlement/cracking due to base oil choice
Viscosity modifier*, 1 or 2	2–15%	VI improver and shear stability
Base oils	80–95%	Good oxidative stability and low-temperature fluidity

*as concentrate

Dispersants: Together with providing cleanliness and dispersing sludge, dispersants play a key role as a friction modifier in driveline fluids. They are:

- historically based on those used in common engine oils,
- the single largest component in the additive system, 40–70% weight,

- PIB succinic anhydride, PIBSA, reacted with ethylene diamine derivatives, MW 1000, with TBN ~ 25 mg KOH/g,
- sometimes borated with boric acid for antiwear boost,
- reacted end groups and degree of basicity significantly affect frictional characteristics of dispersant,
- sensitive to the effects of end groups and basicity on their functional characteristics.

Detergents: Together with maintaining cleanliness, detergents are multifunctional:

- historically based on crankcase detergents,
- now almost exclusively 300 TBN synthetic calcium sulphonate,
- sometimes borated with boric acid for antiwear boost,
- a key component affecting dynamic and static friction levels and durability,
- a cause of clutch glazing, so there are limitations on amount that can be used in a formulation.

Oxidation Inhibitors: To slow down the degradation process by inhibiting oxidation. They are commonly a combination of di-nonyl diphenylamine and phenolic compounds:

- detergents supplement the inhibition process by neutralizing acidic by-products,
- the inhibitors used are essentially inert regarding their impact on other fluid properties.

Anti-wear Components: These are, quite often, the most difficult component for the formulator when trying to achieve and maintain the ideal friction curve. Therefore, selection of the right type and level is critical:

- they are almost exclusively organic phosphates and phosphites, which act by forming a phosphate-oxide reaction layer,
- borated dispersants and detergents can be used as supplementary antiwear components,
- di-mercapto-thiadiazoles can also be used as supplementary antiwear components, being particularly effective in reducing micro-pitting.

Friction Modifiers: These components have the biggest influence on friction level and durability and are the key performance differentiator between ATFs. A minimum of two is used to provide:

- initial/breaking-in friction, e.g. ethoxylated amines, glycerol mono-oleate,
- long-term friction durability, e.g. zinc oleate, octadecenamides, long-chain esters (borated).

Other Components: In addition to the major components described above, these include:

- *Antifoams*, as combinations of high and low molecular weight polydimethylsiloxanes,
- *Corrosion Inhibitors*, using mercapto-thiadiazoles which also give an extreme pressure/antiwear boost,
- *Seal Swell Agents*, as sulphurized esters, but which can affect frictional characteristics at high levels,
- *Viscosity Modifiers*, as polymethylacrylates, affecting low-temperature viscometrics and shear stability.
- *Base Oils* – the major component by mass or volume, from Groups I, II, III, IV and V hydrocarbons.

10.7.3 Manual Transmission Fluids

The manual gearbox components requiring protection by a lubricant include:

- the synchromesh ring, requiring yellow metal corrosion protection if sintered or brass,
- the synchromesh ring and cone, requiring the correct level of friction and friction stability,
- dog teeth fatigue and wear, to hold and lock the sliding collar and meshed gear together,
- sliding collar and splined hub, for fatigue and bearing wear,
- constant mesh gears, for fatigue and wear under high load and rolling/sliding forces.

Key performance requirements of the lubricant are:

- oxidative and thermal stability,
- antiwear and load-carrying capacity,
- compatibility with seals to prevent leakage,
- shear stability to resist the high shearing forces.

Wear protection depends on the lubricating film quality, which can be physical or chemical, usually a combination of the two. Physical films, which are somewhat temporary, result from the lubricant's wetting ability with/without a friction modifier. Chemical films are more permanent, resulting from reaction of lubricant chemicals with the metal surfaces. The viscosity of a gear oil is directly related to its film forming ability, hence load-carrying capacity. The higher the load-carrying capacity of the fluid, the greater the protection against wear. Therefore, high-viscosity oils minimize wear.

Typical manual transmission fluids' additive packs contain 6–10 components, many being the same components used for modern automatic transmission fluids. The key differences are the treat levels of components, e.g. dispersants and friction modifiers, and the type and level of antiwear components. A typical manual gearbox standard operating temperature of 90°C is not as thermally challenging as that of a modern automatic transmission in excess of 120°C. This is usually reflected in the superior oxidative stability exhibited by modern automatic transmission fluids compared with manual transmission fluids. Table 10.3 shows the generic composition of a manual transmission fluid, with the component(s) that differ from an automatic transmission fluid highlighted.

Table 10.3 Generic composition of a manual transmission fluid

Dispersants (1 or 2)	1–4%	Cleanliness, disperse sludge, friction and wear
Detergents (1)	0.0–3.0%	Cleanliness, friction, corrosion inhibition
Anti-oxidants (1 or 2)	0.3–1.0%	Control oil thickening, prevent varnish and deposits
Antiwear (1)	0.5–1.0%	Protection of gears
Friction modifiers (1 or 2)	0.0–0.5%	Controls gear shift feel and synchronizer friction durability
Corrosion inhibitor (1)	0.2–0.5%	Prevent corrosion, rust, pitting and wear
Antifoam (1)	50–300 ppm	Prevent excessive foaming and air entrainment
Seal swell agent	0.3–1.5%	Combats seal embrittlement/cracking due to base oil choice
Viscosity modifier (1 or 2)	2–15%	VI improver and shear stability
Base oils	85–95%	Good oxidative stability and low-temperature fluidity

10.8 Main Functions of an Axle Lubricant

10.8.1 Introduction

An axle lubricant must be able to:

- resist high shearing forces in the gears and bearings,
- give extreme pressure protection,
- prevent foaming,
- resist oxidation,
- prevent wear,
- protect seals,
- suppress noise and vibration.

Limited slip differentials contain clutch plates, which require the correct friction performance to prevent noise and ‘squawk’.

10.8.2 Axle Additive Packs

Axle additive packs typically contain 6–8 components; again a typical axle lubricant additive pack may contain many of the same components seen in automatic or manual transmission packs. The key differences lies in the need for an extreme pressure component, for which sulphurized isobutylene (SIB), polysulphides or xanthates are commonly used.

The axle lubricant should be suited to the type of metallurgy of the components as these vary depending on the axle design and the manufacturer because:

- machining tolerances have improved over the years through the use of PC-controlled and laser-guided cutting tools,
- the grinding finish affects the gear tooth resistance to micropitting. The slide-roll ratio not only affects micropitting but, under high loads, can cause scuffing,
- surface roughness produces higher stresses below the surface, resulting in micropitting,
- finish can aid smooth running and lead to less wear.

The surface finish of the axle also has a major impact on the type of axle lubricant that is needed to protect it. The art of the formulator is to balance the level and type of extreme pressure components to ensure adequate initial protection and to also ensure longevity. Extreme pressure components are invariably oxidatively unstable to their high surface activity; consequently axle lubricants generally have the poorest oxidative stability of all driveline fluids. A ‘typical’ axle lubricant set of components is given in Table 10.4.

Table 10.4 A typical axle lubricant composition

Additive	Treat rate	Function
Dispersants, 1 or 2	1–4%	Cleanliness, disperse sludge (seals) and wear
Detergents, none		
Anti-oxidants, 1	0.3–1.0%	Control oil thickening, prevent varnish and deposits
Antiwear, 1	1.0–2.0%	Protection of axles
Extreme pressure, 1	3.0–5.0%	
Friction modifiers, none		
Corrosion inhibitor, 1	0.2–0.5%	Prevent corrosion, rust, pitting and wear
Antifoam, 1	50–300 ppm	Prevent excessive foaming and air entrainment
Seal swell agent, 1	0.3–1.0%	Combats seal embrittlement/cracking due to base oil choice
Viscosity modifier, 1	2–15%	VI improver and shear stability
Base oils	85–95%	Good oxidative stability and low-temperature fluidity

10.9 General Trends and Emerging Technologies

10.9.1 Transmission Types

Current transmission technology consists of five configurations:

Manual: The driver operates an H-shaped gear lever gate to change the position of the gear shaft inside the transmission. Dependent on the number of pinions on the gear shaft, four, five or six, a corresponding number of gear changes can be made. The earliest motor vehicles employed a manual transmission, and the system remains widely popular in Western Europe. The three main trends in manual transmission development have centred on easing the change action between gears, increasing the number of gear ratios and optimizing the transmission system size.

Automated Manual Transmission (AMT): The driver pushes or pulls a gear lever; some alternative systems also have paddles behind the steering wheel, to change gears up or down. The mechanism within the transmission is the same as in a manual transmission but has an electronic control unit (ECU) fitted. This system has been offered as a halfway solution between manual and automatic transmissions but has not really lived up to expectations. This is because of their relatively poor performance in terms of fuel efficiency and, more importantly, because of the delay that occurs when changing gears. The rather low acceptance level of AMTs so far has also not helped to lower the cost of the technology. Examples of passenger cars equipped with AMT include the Citroën C3, with the Sensodrive system, and the Alfa Romeo models, with Selespeed technology.

Automatic: Most modern automatic transmissions comprise an ECU and a gear shaft. The clutch, which in the other types of transmission operates between the engine and the gears, is replaced by a hydraulic torque converter. Although manufacturers of automatic transmissions have to deal with the problem of size, most of their development efforts have essentially focused on refining the torque converter in order to make it smaller and more efficient. In addition, they have added more gears and developed more sophisticated ECUs to tailor the transmission's performance to the driver's preference. Mercedes recently launched its 7G-Tronic system on the S-Class model and followed the trend of developing automatic gearboxes with more speeds, set by German supplier ZF Friedrichshafen. BMW fitted the 7-Series with a six-speed longitudinal automatic gearbox. Japanese supplier Aisin AW has done likewise by developing the first transverse six-speed automatic transmission for the Audi TT.

Continuously Variable Transmission (CVT): A belt and variable-diameter pulleys in the transmission system allows the gear ratios to continuously vary between a minimum and a maximum value. The transmission is therefore fully automatic from the driver's point of view with no gear changing. Some systems offer an automated manual mode with four or five gears where some ratios are predetermined and the driver changes from one to another by pulling or pushing a lever. Thanks to their relatively small size, CVTs are particularly suited to small vehicles. Overall, CVTs should grow in markets already used to automatic transmissions. Nissan will propose its X-Tronic CVT on the Murano model, and BMW plans to equip its upcoming BMW 1-Series with a CVT system called 'Steptronic'. However, this promising technology has been criticized for its poor operating performance, and GM has decided to drop the technology altogether.

Double-Clutch Transmission (DCT): The Volkswagen (VW) Group was the first carmaker to mass-produce a DCT and commercialize it on one of its models. It offered its Direct Shift Gearbox, DSG, on the Audi TT Quattro at the end of 2003 in collaboration with BorgWarner. This new technology is fairly close to the manual transmission but has two gear shafts instead of one, which allows an almost instantaneous gear change and prevents any energy loss whilst the clutch is disengaged. The DCT is the perfect response to the gear change limitations encountered in the automated manual transmission and represents the most important recent innovation in the transmission system sector. Furthermore, the DCT reduces a vehicle's fuel consumption, which in turn lowers emissions. The only drawback at present of the DCT technology remains its relatively high price.

10.9.2 Current Situation

There are large regional differences in the market penetration of each transmission system. Although the following analysis is based on production, rather than regional sales figures, and therefore includes a proportion of vehicles that are actually sold on export markets, this highlights clear regional inclinations toward a specific transmission type:

- In 2003, 90% of light vehicles produced in the United States were equipped with automatic transmissions. Manual transmission's share remained stable at about 9.5%, whilst CVT has only just appeared in the US market.
- Meanwhile, in Western Europe, the majority, or about 80%, of light vehicles produced were fitted with manual transmissions. Automatic transmissions share increased marginally to almost 15% and alternative transmission systems, more specifically Automated Manual Transmissions (AMTs), were making decent progress, while DCTs had just been launched.
- Light vehicles manufactured in the Japan/Korea region in 2003 were predominantly equipped with automatic transmissions (64%), whilst manual transmission's share remained stable at 28% of total output. It is worth noting that this region had the largest share of CVTs at over 7%.

Over the next 5 years, the automatic transmission has the greater scope for expansion in the main manufacturing areas because it is already predominant in the United States and Japan/Korea and has good prospects in Western Europe. However, it is interesting to observe that, on a global basis, it is manual transmissions that will make the most noticeable progress, fuelled by the expected increase in vehicle output in emerging markets and more particularly in China, where low-technology cars prevail and the automatic transmission remains too expensive an option.

Chapter 11
Aviation Lubricants

A.R. Lansdown and S. Lee

Abstract Aviation lubricants must be extremely reliable, withstand high specific loadings and extreme environmental conditions within short times. Requirements are critical. Piston engines increasingly use multi-grade oils, single grades are still used extensively, with anti-wear and anti-corrosion additives for some classes of engines. The main gas turbine lubricant problem is transient heat exposure, the main base oils used are synthetic polyol esters which minimise thermal degradation. Aminic anti-oxidants are used together with anti-wear/load-carrying, corrosion inhibitor and anti-foam additives. The majority of formulation viscosities are 5 cSt at 100°C. Other considerations are seal compatibility and coking tendency.

Aviation hydraulic fluids are divided into military, mainly PAO based, and civil aircraft which are mainly phosphate ester based. The first contains anti-oxidant, anti-wear and seal compatibility additives, the second prefers trialkyl over triaryl phosphates and contains anti-hydrolysis additives. Aviation greases are subject to extreme operating conditions, such as high-temperature conditions up to 550°C in wheel bearings and resisting water ingress. Airframe and wheel bearing greases are of two types, either lithium soap/complex or clay based. Helicopter transmission lubricants serve the most critical gears in aviation, carrying power for both thrust and lift. Ester-based lubricants are either the same grade as the engine, or a different engine lubricant grade, or a grade intended specifically for helicopter transmissions.

11.1 Introduction

Three factors dominate all aspects of aircraft design. First, the need for the highest possible reliability due to the inherent higher risk and potentially catastrophic consequences of in-flight failure. Second, the need to minimise weight and volume of all components, resulting in high specific loading in all mechanisms. Therefore, there is high specific power dissipation so that operating temperatures are high. Third, the extreme range of environmental conditions encountered from –60°C on the ground, or –80°C in the stratosphere, to over 200°C skin temperatures in supersonic aircraft. Pressures can range from over 1 bar down to less than 10 mbar [1]. An example is

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aircraft wheel bearing grease which can be subjected to a cold soak during long-haul flights but then rapidly subjected to high temperatures generated by the brakes on landing.

Because of these factors, the lubrication requirements of aircraft are generally very critical. Only in a few cases can lubricants developed for non-aircraft applications be used satisfactorily in aircraft. This has not always been the case; the mineral oil or castor oil lubricants used in the earliest aircraft were all standard automotive or marine products.

World War I led to the recognition of the need for special lubricants in aircraft engines [2]. Previously, aircraft rarely climbed to higher than a few thousand feet and engine mechanical reliability was so poor that lubricant reliability was not a limiting factor. But by 1918 aircraft were flying regularly as high as 18,000 feet and flights often lasted up to 5 h. High-altitude flights brought problems of low temperatures resulting in the need for highly refined lubricants with good viscosity–temperature characteristics. The long flights necessitated clean oils with low deposit formation.

Castor oil lubricants in rotary engines gave no problems, for reasons explained later, but long-range bombers and flying boats did not use rotary engines and their needs led to a steady improvement in engine lubricant quality.

The divergence between ordinary automotive engine lubricants and aircraft engine lubricants widened during the 1930s when there was a steady increase in the use of additives in automotive lubricants. Additives were considered undesirable for aircraft use and aircraft engine lubricants remained largely additive free.

The introduction and development of gas turbine engines led to the development of new lubricants. While the early gas turbine engines ran successfully on mineral oil lubricants, and in fact many Russian aircraft engines still operate on such lubricants, the demand for higher specific thrust, with the concomitant high operating temperatures, needed lubricants with better thermal stability. Carboxylic esters were developed which, with yet further improvements, are still used today. These lubricants are also used in aero-derived industrial and marine gas turbines, meaning that for the first time lubricants developed for aircraft were used in other applications.

Lubricant technology has now advanced to the stage where the conditions experienced in operating engines can be accurately reproduced in test rigs. This allows aircraft gas turbine lubricants to be developed to such an advanced stage that the final approval often takes place in aircraft in commercial service.

Recognition of the critical nature of aircraft lubrication brought a need for detailed specifications to control the quality and performance of the lubricants. For 50 years practically all lubricants have had to meet stringent specification requirements. The great expansion of international air transport after 1945 and the formation of major military alliances led to great pressure to standardise aircraft fuel and lubricant specifications. The logistical problems of supplying large numbers of different lubricants, and the potential hazards of using the wrong lubricant, have also led to great efforts to reduce the number of lubricants permitted to be used in aircraft. The end result is that most aircraft lubrication requirements are now met by a relatively small number of closely controlled high-quality products, although there are still a comparatively large number of speciality greases in use.

11.2 Piston Engine Lubricants

11.2.1 Lubrication of Rotary Engines

In the aviation context, the term 'rotary engine' refers to the class of reciprocating piston engines where an assembly of radially mounted cylinders rotates around a stationary crankshaft. Strictly, such engines should be referred to as 'rotating-radial engines', but 'rotary engines' have become the accepted term, an example is shown in Fig. 11.1. Rotary engines were a major factor in aircraft propulsion for only 10 years, but during that short period they made a vital contribution to World War I military aviation. The first aircraft rotary engine was a seven-cylinder Gnome used by Louis Paulhan in a Voisin in June 1909 [3]. By 1917 they were used in thousands of many of the best British and French scout (fighter) aircraft. By 1925 production had virtually ceased, although some remained in service until about 1930.

Because of the difficulty in providing a controlled lubricant supply to the rotating cylinder assembly, lubricant was supplied in the fuel feed. High centrifugal forces caused rapid lubricant loss from the piston/cylinder interface so that the technique of dissolving a mineral oil in the fuel, as in modern small two-stroke engines, would leave an inadequate oil film on the cylinder walls. Standard practice used a vegetable

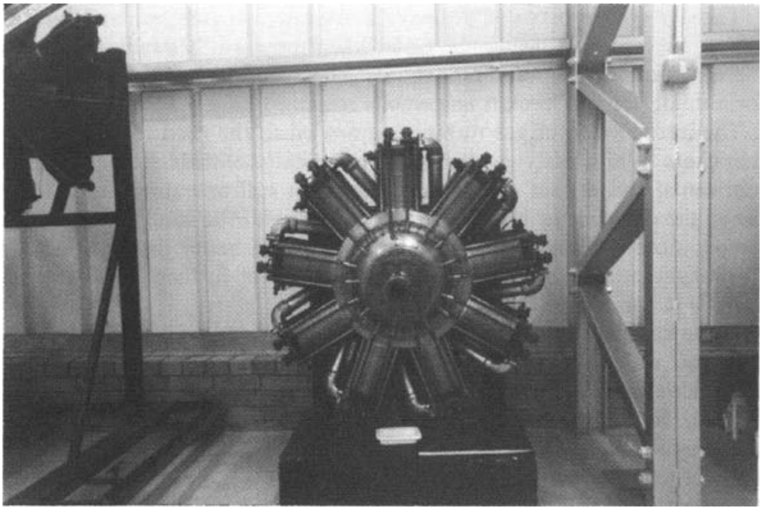


Fig. 11.1 Bentley, BR2 rotary engine (courtesy of Scottish Museum of Flight)

oil, insoluble in the fuel, and castor oil was the usual choice. The castor oil concentration in the fuel was as high as 30% to overcome rapid lubricant loss. Castor oil and other vegetable oils have very good boundary lubrication characteristics and the standard of lubrication in all the engine components was generally good. These lubricants have the disadvantage of poor thermal and oxidative stability.

The lubricant supply in rotary engines was a 'total loss system' and consumption was very high. The most economical engines, built by the Le Rhone company, consumed oil at about 4 l/h for a 90 hp engine. Resulting from this high consumption, the rapid degradation of the lubricant itself was not a problem but the engine surfaces were rapidly lacquered with varnish-like films of polymerised degraded lubricant. A beneficial side effect of such films was very effective corrosion protection and some rotary engines have been found in perfect operating condition after 70 years or more of disuse. Small quantities of aviation-grade castor oil lubricant are still manufactured, such as Castrol R40, for use in the small number of antique rotary-engined aeroplanes still able to fly.

11.2.2 Lubrication of Conventional Aircraft Piston Engines

Apart from the rotary engines described above, piston engines can all be classified as radial or in-line. In-line engines may have either one bank of cylinders, horizontal or vertical, or they may have two or more banks in various arrangements, Fig. 11.2.

Radial engines may have one, two or four rings of cylinders, each containing between three to nine cylinders mounted radially about an axis parallel to the direction of flight, Fig. 11.3, with always an odd number of cylinders in each ring.

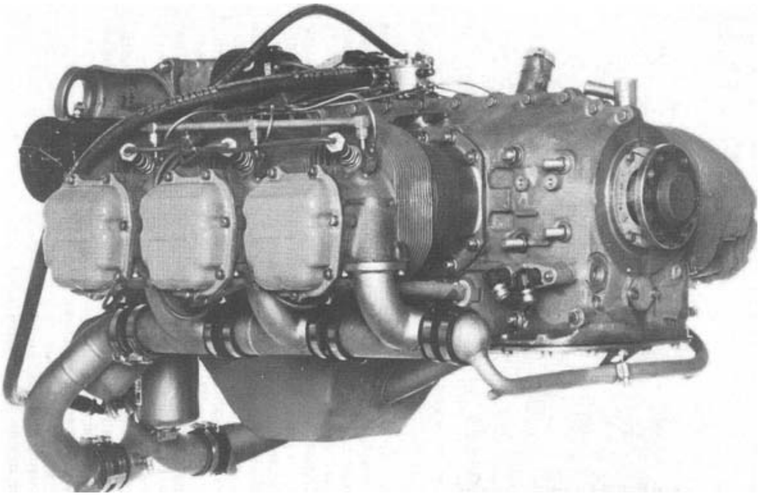


Fig. 11.2 Continental 6-cylinder in-line engine (courtesy of Teledyne Continental Motors)

Fig. 11.3 Jacobs radial engine, installed in a Morane-Saulnier MS.505 (courtesy of Scottish Museum of Flight)

Weight minimisation led to increases in the power/weight ratio of piston engines from 1:3/1:4 hp/lb in 1918 to over 1:1 for the Rolls-Royce Merlin and Bristol Centaurus engines by 1945. But after the development of successful gas turbines, the use of large piston engines decreased rapidly and by 1970 few piston engines of more than 400 hp were being manufactured.

It is probably next to universal in automotive engines for the lubricant to be contained in a sump which also encloses the crankshaft. This system is not suitable for aircraft engines because turbulence or manoeuvring leads to rapid changes in the magnitude and direction of acceleration. Using a sump is impossible for radial engines. Many aircraft piston engines are therefore lubricated on the ‘dry sump’ principle in which lubricant returning to the crankcase, or other collection points, is removed by scavenge pumps and transferred to a separate tank, usually via a cooler. The lubricant is then fed to the various lubrication points by a pressure pump which has a lower capacity than the scavenge pumps, to ensure that lubricant is efficiently scavenged and does not accumulate in the engine. However, small horizontally opposed in-line engines commonly operate with a wet sump.

The earliest piston engines used either mineral or vegetable oil lubricants and in many cases it is now difficult to find out which was preferred. By 1919 the situation had generally stabilised: castor oil was always used for rotary engines but mineral oil was widely used in other engines while some engines could use either [4].

The choice between mineral oil and castor oil in those early years was not as obvious as now appears. Castor oil has excellent boundary lubrication characteristics and therefore more forgiving of poor design features leading to inadequate hydrodynamic film formation. Less avoidable problems, such as excessive dynamic loading and the temporary problem of restarting a hot engine, also benefited from the better boundary lubrication of castor oil. The boundary lubrication characteristics of mineral oil were inferior to castor oil while their viscosity–temperature characteristics and oxidation resistance were also poor by modern standards. Total replacement of castor oil by mineral oil was not addressed until the 1930s, either for aircraft or automotive use. Even then, castor oil-based lubricants were probably the most widely used in racing and their use, either alone or in conjunction with ester-based lubricants, continued until at least the late 1960s. The growing dominance of mineral oil was due to improved refining, greater availability and lower cost. Improvements in refining made large quantities of clean mineral oils available with good viscosity–temperature characteristics and far better oxidation resistance. These two factors were all-important for the high cylinder temperatures of aircraft engines.

Compared with automotive engines, aircraft piston engines did not suffer from water contamination or low-temperature sludge formation because of their higher operating temperatures. They were less prone to corrosion because aircraft fuels were low in sulphur compared to automotive fuels and oil consumption was relatively high. Their main problems were oxidation and foaming, associated with dry sump operation.

It is important in aircraft engines to avoid solid deposits because the relatively lengthy supply pipes are sensitive to blocking by deposits and the varied motion of the aircraft tends to prevent solids from settling out in the tank. Early lubricant additives tended to produce solid decomposition products and were therefore considered to be unacceptable for aircraft use. Oxidation resistance was ensured by the use of highly refined solvent-extracted basestocks and anti-oxidants were only used for a few particularly demanding engines.

Ashless additive development has reduced the risk of solid deposit formation and ashless dispersants, anti-oxidants and anti-foam agents are now permitted in most engines. Non-dispersant mineral oils are now used primarily for older aircraft and as a running-in oil for new engines or after overhaul.

The viscosity characteristics of the oil are important. High viscosity is needed at high operating temperatures because of high specific power and consequential high bearing loads. Good low-temperature performance is also required because aircraft are often stored outdoors and must be capable of starting after a long overnight soak at low ambient temperatures. The lubricant must have a low pour point as well as good temperature–viscosity characteristics, that is, a high viscosity index. Good viscosity–temperature characteristics are obtained by using highly refined paraffinic basestocks and ashless dispersants can give some viscosity index improvement. In spite of this, oil viscosity at low temperatures is usually too high to allow the engine to respond satisfactorily when increased power is required. It may even be too high for the engine to be started at all and leads to several constraints on engine operation:

(i) many piston engines must be run at low power after starting until a specified lubricant temperature is reached, above which engine power can be increased,
(ii) in an extended glide descent, the power must be increased at regular intervals, commonly every thousand feet of descent, to warm up and circulate the oil. Failure to do this can result in the engine failing to respond when power is required at the end of the glide. Many forced landings, and even crashes, have resulted from this,
(iii) it may be necessary to operate the propeller pitch control at regular intervals with an aircraft using either constant speed or variable pitch propellers in a cold environment at a steady speed and power setting. If this is not done, the small volume of oil present in the pitch change mechanism may become too viscous to flow when pitch change is again required,
(iv) where air temperatures are very low and there may be doubt about whether an engine can be restarted after a shutdown, many different techniques are used to warm either the oil or the engine. One procedure is to dilute some or all of the lubricants in the engine with petrol before shutting down. Using lubricant dilution makes it necessary to carefully warm up the engine on re-starting to evaporate the petrol before its boiling point is reached in the lubricant tank.

These problems can now be alleviated to some extent by the use of a multi-grade engine lubricant. The use of multi-grade oils, 15W/50 and 20W/50, has continued to grow since their introduction in 1979, but single-grade products still have a strong following in the industry. Single versus multi-grade discussions are still hot topics among pilots and mechanics alike and are frequently the subject of trade publication articles. Some multi-grades are marketed as ‘semi-synthetic’ and some are not – the desirability of synthetic oils in aircraft piston engine oils is also often debated. A separate ‘class’ of products has come to the market that contain a pre-blended supplemental anti-wear additive that meets the requirements of (Airworthiness Directive) AD 80 04 03 R2, paragraph b.1. The AD applies to certain (mostly O-360 family) Lycoming engines that require additional cam and lifter wear protection provided by Lycoming additive part no. LW-16702 (TCP). Anti-corrosion additives are also now included in some formulations to help protect against corrosion during extended idle periods.

11.3 Aviation Gas Turbine Lubricants

11.3.1 Introduction

Aircraft gas turbine engines, otherwise known as jet engines, are simpler in principle than piston engines in their design and construction and also in their lubrication requirements. There are no moving parts in the combustion chambers, so the lubricant is not exposed directly to combustion temperatures. The compressor and the expansion turbine are the main moving parts which are in steady rotation, so the problems of dynamic loading due to reciprocating pistons are avoided.

Despite the relative simplicity of the gas turbine the lubricant still faces serious challenges, the greatest of which is heat. Modern engine bulk lubricant temperatures can range between 80 and 100°C for the system oil feed and peak at approximately 190°C on the scavenge side, with exposure to metal wall temperatures in the bearing chambers between 300 and 400°C. Combining this with the aircraft operators desire to extend the time between major overhauls even further, currently in excess of 40,000 operating hours for some civil engines, then the enormity of the challenges these lubricants have to face becomes apparent. It is granted that a single charge of lubricant is not expected to last for that period, as lubricant is lost during operation and regularly topped-up with fresh lubricant. The equilibrium of used lubricant/new lubricant that is reached must keep the engine lubricant system components sufficiently clean throughout this period. Although there are no combustion products for the lubricant to deal with, it can still form coke deposits because of the high transient temperatures experienced. Any such deposits must be prevented from building up to the point at which they cause a blockage. The lubricant still has an important part to play in minimising the formation of these deposits in the first place and be able to efficiently remove those that are formed. The thermal stability of turbine engine lubricants is probably the single greatest challenge for both engine builders and oil formulators at present.

All gas turbine engines have three basic components: first, an air compressor to supply air under pressure to the combustion chambers; second, the combustion chambers themselves and third, an expansion turbine driven by the combustion gases. The energy from the expanding combustion gases is greater than required for the compression process and this is the basic principle of operation of the gas turbine engine. The excess energy is used partially to power the engine and aircraft accessories, e.g. fuel pumps, lubricating oil pumps and electric/hydraulic power. The remainder of the excess energy produces the high-velocity efflux of the jet resulting in the thrust experienced by the engine. The arrangement of the three components is most clearly seen in an early turbo-jet such as the Rolls-Royce Nene, Fig. 11.4.

Modern gas turbine engines are conveniently divided into three classes. The earliest successful aircraft gas turbine engines were the true jet engines, more specifically called turbo-jets. In these engines the whole of the propulsive force is provided by the jet thrust and the turbine is designed to extract only enough power to drive the compressor and some auxiliary components.

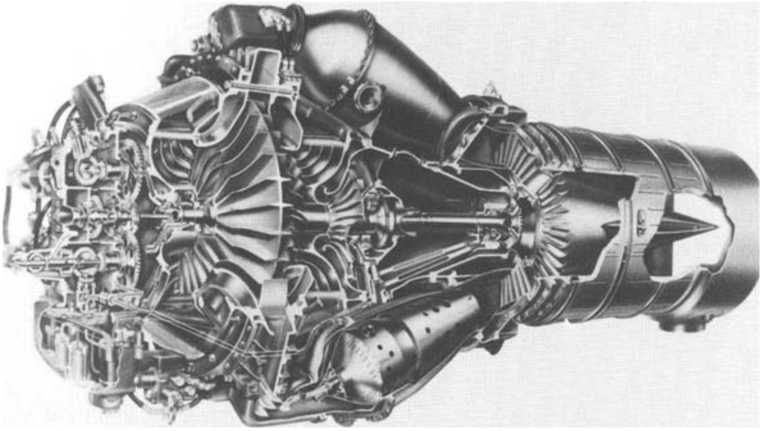


Fig. 11.4 Sectioned view of a Rolls-Royce Nene turbo-jet (courtesy of Rolls-Royce plc)

The second class is the turbo-props, or prop-jets, where the turbine is designed to abstract a high proportion of the power from the combustion gases to drive a propeller which provides virtually all of the propulsive force, an example is shown in Fig. 11.5. Turbo-props are much more economical than turbo-jets at aircraft speeds below 450 mph where propellers themselves retain their efficiency. The gas turbines used in helicopters are similar in some respects where the bulk of the power is abstracted by the turbine to drive the rotors.

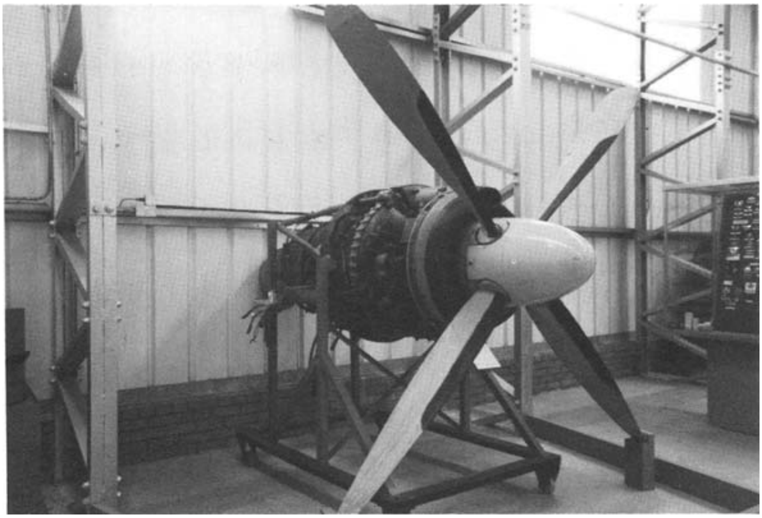


Fig. 11.5 Rolls-Royce Dart 506 turbo-prop (courtesy of Scottish Museum of Flight)

The third class of gas turbine includes the ‘high bypass’ and ‘fan’ engines, jointly classified as turbo-fans where the turbine abstracts more power than required simply to supply compressed air to the combustion chambers. The surplus is used to drive a low-pressure compressor to supply additional airflow which is the core of the engine, that is, the part of the engine containing the combustion chambers. This low-velocity airflow is ducted to surround the hot jet efflux and helps to minimise noise emissions from the engine. Like the turbo-jets, these engines are most effective at high airspeeds but are more economical than the turbo-jets. Figure 11.6 shows an example of a turbo-fan engine.

Fig. 11.6 Rolls-Royce RB211-525E4 turbo-fan engines, installed in a Boeing 757 (courtesy of Rolls-Royce plc)

In addition to lubricating the engines, turbine lubricants are also required to lubricate a number of associated systems such as auxiliary power units and constant speed drive units and to act as hydraulic fluids, for instance, in the propeller pitch control units of some turbo-props.

11.3.2 Base Oil Technology

Lubricants for the early gas turbine engines were essentially highly refined mineral oils, a natural extension from the piston engine lubricant technology available in the early 1940s. Such an oil is still specified today in Defence Standard 91-99, UK MoD Grade OM-11 [5] and consists of ‘pure refined mineral oils with 0.05–0.10% stearic acid’ to enhance load-carrying/anti-wear and anti-corrosion properties. It can also contain an anti-oxidant which, in common with many mineral-based fluids, is the ‘hindered phenol’ type, Chapter 4. Although not in widespread general use as a gas turbine lubricant for many years it was still used by the RAF in the Rolls-Royce Avon engines of the Canberra aircraft until 2006.

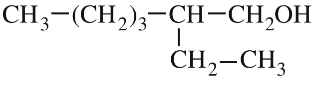
However, rapid development of the gas turbine engine and the quest for greater power resulted in higher operating temperatures of the lubricated components and the mineral-based lubricants of the day could not withstand such temperatures for sufficient lengths of time. The UK and the USA made no real effort to develop mineral-based lubricants further. The Soviet Block has continued development of mineral-based lubricants, some of which are still in use today in Russian aircraft. However, this chapter concentrates on those lubricants developed and used in western aircraft engines.

In the UK and the USA the focus for lubricant development turned to ester-based synthetic lubricants. In the 1930s and 1940s German scientists, led by Professor Zorn, had conducted research into using di-esters and polyol esters as lubricants. Compared with mineral lubricants, ester-based lubricants had better thermal and oxidative stability in addition to good low-temperature properties without the need for pour-point depressant additives. In the 1950s both the UK and the US militaries produced specifications for turbine lubricants based on di-esters. The UK initially concentrated development on lubricants for turbo-props where the load-carrying requirements of the reduction gears used in these turbo-props required a higher viscosity lubricant. This led to the development of a polyglycol ether-thickened 7.5 cSt at 100°C lubricant. The USA focused on turbo-jets to develop a 3 cSt lubricant. Despite the differences in viscosity, both lubricants were based on di-ester technology.

The main esters used in the manufacture of di-ester-based turbine lubricants are based on di-basic acids such as:

Sebacic acid	$HOOC{-}(CH_2)_8{-}COOH$
Azelaic acid	$HOOC{-}(CH_2)_7{-}COOH$
Adipic acid	$HOOC{-}(CH_2)_4{-}COOH$

which are reacted with alcohols to produce the di-esters. The choice of both acid and alcohol has a marked effect on the properties of the finished product. As an example, the longer chain di-acids improve the viscosity index, VI, but reduce the pour point. An alcohol commonly used is octanol, $CH_3{-}(CH_2)_7{-}OH$. If used as *n*-octanol, this raises the di-ester pour point to an unacceptable degree. However, using the 2-ethyl hexanol isomer:

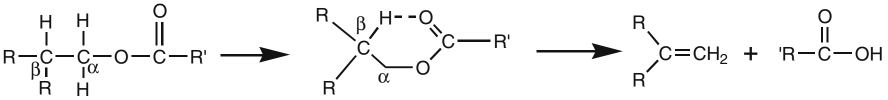


$$CH_3{-}(CH_2)_3{-}\underset{\displaystyle CH_2{-}CH_3}{\underset{|}{CH}}{-}CH_2OH$$

gives a marked reduction in pour point while maintaining an acceptable VI and is therefore commonly used in the formulation of di-ester base oils.

The properties of the base oils are, of course, enhanced by additives in the finished product. Apart from the polyglycol thickener used in the 7.5 cSt di-ester-based lubricant most of the additive types used in di-ester-based lubricants are also used in the polyol ester-based lubricants, discussed later in this chapter. The resulting di-ester lubricants were suitable for the maximum bulk oil, 149°C, and bearing, 204°C, temperatures encountered in 1950s gas turbine engines [6].

Despite the addition of anti-oxidants, di-ester-based lubricants are limited in their high-temperature capabilities by a β-hydrogen abstraction. The structure of the di-ester molecule allows it to form a hydrogen-bonded, six-membered, ring. This results in the breakdown of the molecule into an alkene and aldehyde, which then leads to further chemical breakdown as follows:

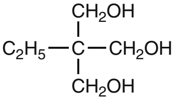


(Reaction sequence 11.1)

It is important to note that the alkenes produced in reaction (11.1) can eventually form particulates in the lubricant, a critical criterion used in oxidative stability tests to determine the capabilities of turbine lubricants. This is demonstrated by the oxidative stability test [7] used in the Defence Standards for UK MoD gas turbine lubricant grades OX-7 [8] and OX-26 [9].

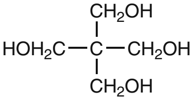
This test involves heating the lubricant in a test tube for 192 h with 250 ml/min of air bubbling through it. Among other properties, the toluene insolubles are determined at the end of the test. The test is repeatedly run at increasing temperatures until the insolubles content increases over that of the unused oil by 0.05%. The OX-7 specification limit, defining the performance requirements of 3 cSt di-ester-based oils, is 190°C minimum. The limit for OX-26, defining the performance requirements of 5 cSt polyol ester-based lubricants, is 210°C. Based on the kinetic principle that the rate of reaction at least doubles for every 10°C incremental rise in temperature, this is a significant gain in performance. Improvements in lubricant formulation now mean that modern 5 cSt polyol ester turbine lubricants tend not to produce any toluene insolubles at all in this test even at higher temperatures.

Polyol or hindered esters prevent β-hydrogen abstraction by eliminating the β-hydrogen. These are manufactured by reacting polyhydric alcohols such as neopentyl glycol, trimethylolpropane and pentaerythritol with mono-acids ranging from pentanoic, $n\mathrm{C}_5$, to decanoic, $n\mathrm{C}_{10}$ [10]:



$$C_2H_5-C(CH_2OH)_3$$

Trimethylol propane



$$HOH_2C-C(CH_2OH)_3$$

Pentaerythritol

Development of higher thrust, and therefore hotter, engines needed a lubricant with improved thermal and oxidative stability. Therefore, lubricants were formulated based on polyol esters. Modern ester-based gas turbine lubricants consist of approximately 95% base oil and the base oil has a dominant effect on the characteristics of the finished lubricant, in particular:

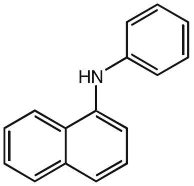
Density
Pour point
Coking propensity
Shear stability
Elastomer compatibility
Viscosity
Thermal stability
Flash and fire points
Lubricity
Acidity
Viscosity index, VI
Oxidative stability
Volatility
Hydrolytic stability
Colour

Ester-based base oils have certain inherent properties such as good VI, and therefore no need of VI improver additives, additive solubility, detergency and dispersancy, an affinity for metal surfaces, and are more biodegradable than mineral oils.

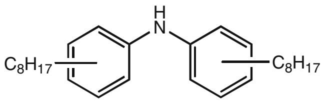
Polyol esters can be designed to enhance specific properties by varying and mixing the alcohols and acids used to manufacture them. But performance improvements in one area can affect performance in another. As an example, the use of shorter, more compact, acids to give a more thermally stable ester molecule can have an adverse affect on elastomer compatibility. The compact ester molecule can more readily penetrate the elastomer matrix, resulting in greater seal swell. Lubricant additives that are aggressive to elastomers can then also penetrate the swollen elastomer and accelerate its breakdown. Another potential disadvantage is with altering VI and lubricity, where using acids with longer alkyl segments improves lubricity and VI but adversely affects oxidative and coking stability. Acids with higher molecular weight reduce lubricant volatility but adversely affect low temperature viscosity. The ester designer must have a clear picture of the main priorities for the finished product.

11.3.3 Anti-oxidant Additives

Anti-oxidants, AOs, for ester-based turbine lubricants are of the hindered amine type, as described in Chapter 4. Commonly used anti-oxidants are phenyl-α-naphthylamine, PAN, octylphenyl-α-naphthylamine, OPAN, and dioctyldiphenylamine, DODPA, and derivatives thereof. Phenothiazine was a common anti-oxidant in the early years of ester-based turbine lubricants but although effective it formed particulates when the lubricant became oxidised. Since particulate formation is a major limiting factor for an engine manufacturer the use of phenothiazine stopped. Phenyl-β-naphthylamine was also used in early lubricants but its use was subsequently banned when it was found to be harmful.



Phenyl-α-naphthylamine

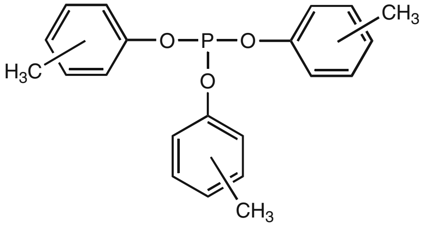


Dioctyldiphenylamine

Two or more different anti-oxidants are commonly used in turbine lubricants because of a synergistic effect giving greater protection at a given treatment concentration than would be achieved for the same concentration of a single anti-oxidant. The quest for increased oxidative and thermal stability has seen the introduction of combinations of oligomeric and monomeric amine anti-oxidants as anti-oxidant packages, the bulkier oligomeric anti-oxidant molecule giving greater stability. Another recent innovation is the use of monomeric anti-oxidants which form oligomers during the oxidation reaction, thus extending the anti-oxidancy of the package beyond the initial reaction of the anti-oxidant. One disadvantage of modern anti-oxidant packages is their tendency to be more aggressive towards elastomers, particularly the older technology types used in engine construction.

11.3.4 Anti-wear and Load-Carrying Additives

As the name suggests these additives are used to reduce component wear and the additive most commonly used is tricresyl phosphate, TCP, usually at concentrations of between 1 and 3% in the finished lubricant. TCP reacts with the metal surface to form a chemically adsorbed film which comes into play in a boundary lubrication regime, i.e. when there is no longer an elastohydrodynamic, EHD, lubricating film holding the metal surfaces apart. The asperities on the metal surfaces come into contact but instead of the metal surfaces welding and tearing chunks out of each other, the film formed on the surface by the reaction of the TCP is preferentially removed, thus protecting the surface from excessive wear.



Tricresylphosphate

Where extreme pressure properties are required, as in certain engine gearboxes or helicopter transmissions, a lubricant containing a phosphate amine salt-type additive may be used. Although improving the load-carrying capability of the lubricant for gears, it can make the lubricant more aggressive towards certain elastomer types, particularly silicone, and can increase the coking propensity of the oil. Another disadvantage is that in the presence of water, this additive type reacts with unprotected magnesium alloy surfaces to produce a deposit which can build up and eventually shed, resulting in oil filter blockages. If the system is kept dry or magnesium alloy surfaces are sufficiently well protected with an epoxide coating for instance, then the reaction does not proceed.

It has been demonstrated previously that improving lubricant performance in one area can have an adverse impact in another area. This is the case for load carrying: it is generally accepted that additives which improve load carrying in gears tend to increase rolling contact fatigue on bearing surfaces.

Anti-wear and load-carrying additives work by reacting with ferrous metal surfaces. The metal surfaces have to be sufficiently reactive themselves for the additive to work, which is the case with traditional steels such as M50 and M50 NiL but problems are encountered with more corrosion-resistant steels. These steels are designed to be chemically less reactive to inhibit corrosion but this affects the ability of the anti-wear additive to react with the metal surface. It is desirable to use these corrosion-resistant steels in engine design and the quest for an additive system that works with corrosion-resistant steels, without adversely affecting other areas of performance, is currently the subject of much research in the aero-engine lubrication community.

11.3.5 Corrosion Inhibitor Additives

Corrosion in lubricated systems can occur for a variety of reasons including static corrosion of steel components from the ingress of water and also reaction between the lubricant, or degradation products of the lubricant, and the metals in the system. As an example, ester-based lubricants have great affinity for water and can absorb several thousand ppm of water from the atmosphere during extended static periods. During periods of operation when the oil becomes heated the moisture is released from the lubricant into the airspace of the lubricated component. During long or frequent periods of operation this is not usually a problem; however, if the periods of operation are not long enough to expel the resulting moist air then, after shutdown, the water can condense onto the cold system components and cause corrosion.

Some additives used as anti-wear agents can also have anti-corrosion properties such as TCP, sebacic acid and azelaic acid. However, corrosion inhibition is a fine balance of competition with the anti-wear/load-carrying capability of the lubricant. Like the anti-wear additive, the corrosion inhibitor is designed to react with the metal surface. Some corrosion inhibitors specifically aimed at preventing static water corrosion of ferrous metals compete with the anti-wear additive for the metal surface to the extent that the resulting lubricant has poorer anti-wear properties than non-corrosion-inhibited lubricants.

Alloys containing copper can catalyse reactions that degrade base oils and benzatriazole and quinizarin are commonly used as yellow metal deactivators to prevent this.

11.3.6 Anti-foam Additives

Foaming of the lubricant in a system can cause a variety of problems including loss of lubricant through overflowing of the resulting increased foam volume, oil pressure fluctuations because oil pumps cannot effectively pump a foam and also breakdown of lubrication because there is insufficient liquid lubricant to form the critical EHD films. It is therefore important to control lubricant foaming, achieved in turbine lubricants chiefly through adding approximately 2–3 ppm of a high-viscosity silicone-based additive. Dose rate and correct dispersion of the additive are critical because higher dose rates can cause foaming, rather than reducing it.

11.3.7 Specifications

From the above discussions it is clear that formulating gas turbine lubricants is a complex business and also that they can be formulated to favour particular properties over others. It is the user of the lubricant who must define the requirements which the resulting lubricant must meet. Ultimately, the lubricant must perform adequately in the engine but it is totally impractical for every single experimental formulation to be tested in an engine. Therefore there must be a means of conveying the technical requirements which the lubricant must meet, which is the purpose of the lubricant specification.

As with other engine lubricants, viscosity is used to divide turbine lubricants into various grades, not by using the SAE classification system but by the lubricant's kinematic viscosity at 100°C. The grades currently available are 3, 4, 5 and 7.5 cSt. Some of the more common specifications used to define these are shown in Table 11.1.

Table 11.1 Turbine lubricant specifications

Specification	Issuing authority	Viscosity grade	Lubricant class	Typical applications
SAE AS5780	SAE	5	SPC, HPC	TP, TJ, TF
MIL-PRF-7808	US Air Force	3 and 4	n/a	TJ, APU
MIL-PRF-23699	US Navy	5	STD, CI, HTS	TP, TJ, TF
Def Stan 91-94	UK MoD	3	n/a	TJ, APU
Def Stan 91-98	UK MoD	7.5	n/a	TP
Def Stan 91-100	UK MoD	5	High load	TJ
Def Stan 91-101	UK MoD	5	STD	TP, TJ, TF

Key: SPC = standard performance capability, HPC = high-performance capability, STD = standard, CI = corrosion inhibited, HTS = high thermal stability, TP = turbo-prop, TJ = turbo-jet, TF = turbo-fan, APU = auxiliary power unit

The most widely used turbine lubricants, by far, are the 5 cSt grades covered by US Navy specification MIL-PRF-23699 [11] and UK MoD specification Def Stan 91-101 [12]. The lubricants approved to the Def Stan happen to be a subset of those approved to the MIL specification that have passed the additional requirements for operation in the UK military engines.

MIL-PRF-23699 has been the industry standard for 5 cSt lubricants, apart from the high-load-type oils, used by both the US military and the civil aviation world for many years. There is not a single 5 cSt lubricant, again apart from the high-load type, used in western aviation gas turbine engines that has not been tested and approved to this specification. However, activity within the SAE E-34 Propulsion Lubricants Committee over a number of years has led to the development of a new specification, SAE AS5780A [13] which has become the new industry standard, particularly for lubricants used in civil aircraft engines. The reason is that, unlike the military specifications, AS5780A has been developed jointly by the engine OEMs, military specification authorities and lubricant manufacturers and contains most of the requirements of MIL-PRF-23699 and the tests used by the engine OEMs in their civil airworthiness certification processes. Also, rather than lubricants being granted certification by a single military authority a body known as the Qualified Product Group, which involves both military authorities and engine OEMs, has been appointed to manage the AS5780A certification process.

All of the above specifications define the performance of the lubricant as much as possible through the use of laboratory-based tests. These range from simple internationally standardised tests such as kinematic viscosity by method IP 71 [14], to complex rig tests such as the US Navy Bearing Coking Rig [15]. Some of the more important of these properties and tests are discussed below.

Coking propensity: The coking propensity of a lubricant is its tendency to produce carbonaceous deposits when exposed to high temperatures. Increased engine power and efficiency have been accompanied by increased oil system temperatures. Also, engine operators want engine overhaul periods to be extended as far as possible, meaning that even if engine temperatures remained constant the lubricant would still be challenged to maintain system cleanliness for increasingly long periods. Therefore, lubricant coking propensity is a major design limiting factor for engine builders.

There are numerous different scenarios under which these deposits can form and as a result, over the years a number of methods have been developed to attempt to simulate these scenarios. Example include ‘thin film coking’ where the lubricant is present as a thin film on a heated surface, ‘oil mist coking’ where an oil mist impinges on a hot surface and ‘puddle coking’ where the lubricant is present as a pool of oil on a hot surface. Developing a method that accurately simulates the coking propensity of a lubricant in an engine is difficult because of these various different scenarios. The problems encountered with coking in one manufacturer’s engine may not be the same as the coking problems encountered in another manufacturer’s engine. Therefore methods have often been developed in-house to investigate specific problems and have not found their way into most of the specifications listed above. However, two methods have gained widespread acceptance, the US Navy’s Bearing Coking Rig and the Hot Liquid Process Simulator (HLPS) [16].

The Bearing Coking Rig is one of the major lubricant performance tests in the US Navy’s 5 cSt lubricant specification MIL-PRF-23699. Therefore, there is a significant set of historical data associated with this method which is also the closest simulation available to a real-life engine-bearing chamber and is therefore quite complex. The lubricant performance is assessed by visually determining the amount and type of coke formed, the weight of deposits captured on a filter and changes in lubricant viscosity and acidity. It is the lubricant’s performance in this test that essentially determines whether it is an STD or HTS class lubricant, see Table 11.1. The disadvantage is that there is only one of these rigs currently in use.

By contrast, the HLPS is a newer technique, relatively simple and works by passing the lubricant over a pre-weighed stainless steel tube at 375°C for 20 h. The lubricant's coking propensity is then determined by re-weighing the tube and calculating the weight increase. This test is designed to simulate coking in engine lubricant feed pipes. Despite its relative simplicity the major engine manufacturers have agreed that it does discriminate between lubricants of different coking performances and, along with the Bearing Coking Rig, it is one of the main factors in determining whether a lubricant is an SAE AS5780A SPC or HPC class lubricant.

Elastomer compatibility: Turbine lubricants must be compatible with the materials that they contact within engine lubricant systems. One such class of materials is elastomers, mainly as engine oil seals. As previously stated, certain lubricants, particularly those formulated to give higher thermal stability, can be aggressive to certain elastomers. This is not a failing of the lubricant any more than a failing of any specific elastomer type. It should be, and is, recognised as one of the challenges of meeting the demands of modern and future engine designs and operating conditions. Elastomer manufacturers have developed elastomers that are more resistant to degradation by advanced lubricant formulations. These more modern elastomers tend to be fitted to the more modern engines; however, fleet operators like to be able to use the same lubricant across all of their aircraft, so it is important to determine the level of compatibility with both modern and more traditional elastomers. Not all specifications demand the testing for compatibility with the same elastomers but currently the specifications listed above include testing with the following elastomers:

Silicone
Nitrile
Perfluorocarbon
Fluorosilicone
Fluorocarbon
Low compression set fluorocarbon

A variety of different methods are employed but all are based on the same principle – the elastomer is exposed to the lubricant at an elevated temperature, as high as 204°C, for several days. After this treatment, the elastomer is analysed to determine any change in weight, or swell. Most methods also examine other properties of the elastomer to determine the affect on flexibility and/or strength. Several days may not seem very long when considering the time the elastomers and oils spend in the engine between major overhauls. But these tests use accelerated conditions and represent a far higher liquid to elastomer surface ratio than encountered by oil seals in service and are therefore quite a severe test of compatibility.

Corrosion/oxidation: Although corrosion and oxidation are two different properties, they are very much linked in the engine environment. The presence of construction metals in the lubrication system can catalyse lubricant oxidation and the products of lubricant oxidation can cause corrosion of some metals. Therefore, some methods determine these properties in the same test, for instance, Federal Test Method (FTM) 5308 [17], while others look at the oxidative stability of the lubricant in the absence of metals, for instance, Def Stan 05-50 (Part 61) Method 9 [18].

Both methods involve heating the lubricant to temperatures in excess of 200°C with a high volume of air being passed through the sample for extended periods of time. Despite the different approaches both methods assess the effect on the lubricant in much the same way by measuring increases in viscosity, total acid number, TAN, and insolubles content. Method 9 additionally assesses volatility loss and formation of a 'solidus', essentially the point at which the sample no longer flows. FTM 5308 adds the dimension of assessing the effect of the oxidised lubricant on metal test pieces, namely:

Steel
Magnesium
Silver
Copper
Aluminium
Titanium

While some of these metals are not used in the engine in their pure form, e.g. copper, it may be a constituent of an alloy that is used and it would be impractical to try and incorporate every alloy used in engine construction as a separate test piece.

Rather than just assessing the condition of the lubricant at a series of set temperatures, Method 9 attempts to determine the temperatures, for a given test duration, at which the various deterioration parameters reach critical 'assessment levels', e.g. an increase in TAN of 1.5 mg KOH/g. Further tests are then conducted at even higher fixed temperatures to determine the time, or 'effective life' it takes to reach that same assessment level. The result is an extensive set of data relating these assessment levels with time and temperature. The ultimate goal is to construct an Arrhenius plot showing the relationship between effective life and temperature for each deterioration parameter.

Both methods are recognised as having their advantages and their weaknesses and current thinking is that modified or new methodology should be developed that combines the advantages of both, i.e. use of metals and the generation of extensive time/temperature data.

Load-Carrying/Anti-wear Capability: Load-carrying/anti-wear capability is becoming an increasingly important property to be able to measure. This has traditionally been measured using complex gear rig tests, such as the Ryder Gear Machine [19] or the IAE Gear Machine [20], which essentially assess the lubricant performance with highly loaded gears against a reference fluid. However, although gas turbine engines do have gears which primarily drive auxiliary systems, these are not the only parts of the engine where it is important to understand the tribological performance of the lubricant.

Although gear test rigs have traditionally been used, recently ball on disc and ball on cylinder methods have been developed as more economical ways of providing load-carrying/anti-wear data. As stated in Section 11.3.4, what is good for gears is not necessarily good for bearings. This has led to research and development into techniques to determine bearing fatigue. Also, the desire of engine builders to use corrosion-resistant steels in new engine designs has led to considerable research effort into the behaviour of lubricant anti-wear additives with these steels.

11.4 Aircraft Hydraulic Fluids

11.4.1 Introduction

Larger and more complex aircraft usually use hydraulics for most mechanical systems, including flight controls, landing gear, brakes and others. Many of these systems are critical to the safety of flight and the quality of the hydraulic fluid is vital.

The first aircraft hydraulic fluid was castor oil based. Modern aircraft now use one of two broad classifications of hydraulic fluid, hydrocarbon based or phosphate ester based.

11.4.2 Hydrocarbon-Based Hydraulic Fluids

Hydrocarbon-based hydraulic fluids can be subdivided into two categories: those with a mineral base oil which were introduced to overcome the poor low-temperature properties and instability of the castor oil-based hydraulic fluids and those with a polyalphaolefin (PAO) base oil. Both are used extensively in military aircraft.

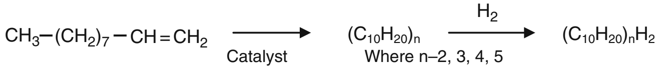
Mineral-based hydraulic fluids are controlled in the USA by military specification MIL-PRF-5606 and in the UK by Defence Standard 91-48 although the resulting grades of product are effectively the same and both are covered by the same NATO designation H-515 [21]. The most widely used fluid has excellent low temperature properties with a maximum pour point of –60°C due largely to the naphthenic nature of the base oil. The fluid also contains:

- not more than 20% of a VI improver, typically polymethacrylate based,
- not more than 2% of an oxidation inhibitor, typically hindered phenol based,
- not more than 0.03% of a copper passivator,
- approximately 0.5% triarylphosphate-based anti-wear agent,
- a red dye for identification and leak source detection.

The low-temperature fluidity requirements of the applications in which this fluid is used mandate a base oil of a relatively light nature which results in a low flash point. The specification requirement is 81°C minimum using the Pensky-Martens closed (PMC) method [22]. The US military concerns for the flammability of this fluid led to the requirement for a less flammable hydraulic fluid. Civil aircraft of the period were already using phosphate ester-based hydraulic fluids because of their fire resistance. But their very different chemistry meant they were incompatible with hydraulic systems developed for the mineral-type fluid and conversion of those systems to accommodate the phosphate ester fluid was considered too expensive.

Also, the phosphate ester fluid did not have the thermal stability required for military systems at that time [23], and for this reason a PAO-based hydraulic fluid was developed [24].

PAOs are synthetic lubricant bases, sometimes referred to as synthetic hydrocarbons, produced by a chemical polymerisation process, typically of 1-decene, Chapter 2. The resulting polymer chain lengths can be tailored to provide the fluid with the physical characteristics required:



$$CH_3{-}(CH_2)_7{-}CH{=}CH_2 \xrightarrow[\text{Catalyst}]{} \underset{\text{Where n–2, 3, 4, 5}}{(C_{10}H_{20})_n} \xrightarrow{H_2} (C_{10}H_{20})_nH_2$$

Compared with the mineral-based fluids, these fluids exhibit reduced variation in viscosity as a function of temperature, which removes the requirement for a VI improver to be added. PAO-based hydraulic fluids also demonstrate outstanding reliability under mechanical stress and excellent chemical and thermal stability. The fluid developed was given the NATO designation H-537 and is controlled by the US military specification MIL-PRF-83282. In contrast to the mineral-based H-515 this fluid has a PMC flash point in the region of 215°C which is a considerable increase.

However, it is also significantly more viscous at low temperature. MIL-PRF-83282 specifies 2200 cSt maximum at −40°C, whereas MIL-PRF-5606 (H-515) specifies a maximum of only 600 cSt at the same temperature. The difference was considered too great for some military aircraft operations and another grade of hydraulic fluid was therefore developed.

After significant development activity at the US Air Force Research Laboratory (AFRL) a fluid based on a PAO dimer/trimer blend was chosen [25]. The fluid was given the NATO designation H-538 and is controlled by the US military specification MIL-PRF-87257. The result is a fluid that has a PMC flash point of in the region of 175°C, a significant improvement over the mineral-based H-515, and a maximum viscosity of 550 cSt at –40°C, thus achieving the goal of reduced flammability while retaining good low-temperature performance.

Hydraulic fluid flammability is a difficult property to assess and flash point demonstrates only one aspect of that flammability, namely the temperature at which, under the conditions of the test, sufficient vapour is produced to generate a flash when a flame is applied to the vapour space above the liquid. Another approach is to determine the flame propagation rate, the rate at which a fire spreads once the fluid has ignited. Typical flame propagation rates for these fluids are stated in Table 11.2 [26]:

Table 11.2 Flame propagation rates for hydrocarbon-based hydraulic fluids

Mineral based	H-515	0.7 cm/s
PAO based	H-537	0.2 cm/s
Low-temperature PAO based	H-538	0.3 cm/s

The higher the flame propagation rate, the faster the fire spreads and therefore the more flammable the fluid, as measured by the test. As can be seen this approach ranks the fluids in the same order as the flash point, with H-515 being the most flammable and H-537 the least. There are a variety of methods that can be used to demonstrate flammability and some show the PAO fluids in a better light than others; however, the ultimate test of flammability has to be the performance of the fluid in service. US Air Force statistics show quite clearly a significant reduction in aircraft losses since the introduction of the PAO-based H-537 into service.

In common with the mineral-based H-515 fluid the PAO-based fluids also contain hindered phenol-based anti-oxidants and TCP as an anti-wear agent but, as previously stated, they do not need the addition of a VI improver [27]. PAOs tend to give very low swell of the elastomer types used in the applicable hydraulic systems. A certain degree of elastomer swell is required to ensure good sealing of the system and therefore the PAO-based fluids contain up to 35% by weight of di-ester to produce sufficient seal swell.

One of the major advantages of these fluids is that they are all compatible with each other in all proportions and with all the aircraft hydraulic systems and hydraulic system materials designed to use any of these three hydraulic fluids. That has enabled transition from one to the other by attrition, i.e. just convert by topping off with the new hydraulic fluid. This saves considerable fluid and maintenance time compared to repeatedly flushing and filling to obtain a high percentage of the new fluid in the aircraft.

11.4.3 Phosphate Ester-Based Hydraulic Fluids

Because of concerns in the 1940s over the flammability of mineral and vegetable oil-based hydraulic fluids the civil aviation industry sought a fluid with greater fire resistance. The result was the introduction of a phosphate ester-based hydraulic fluid. These fluids contain in the region of 90% phosphate ester and are of the general structure $(RO)_3P{=}O$, where $R =$ butyl or isobutyl.

If flash point is used to compare these fluids with the hydrocarbon-based fluids discussed previously, then the phosphate ester fluid would appear to be more flammable than the PAO-based H-537 and approximately equal to the low-temperature PAO H-538. However, it is with the flame propagation rate where phosphate ester fluids have the advantage. In the flame propagation test, the fire from the phosphate esters does not travel the distance in the test and self-extinguishes.

There are two broad categories of phosphate esters, triaryl phosphate and trialkyl phosphate. Although triaryl phosphate-based fluids have superior fire resistance and oxidative stability, the trialkyl phosphates have better viscosity/temperature properties, low temperature viscosity and lower density [26]. Low temperature viscosity and fluid density are major considerations for aircraft designers and excellent low temperature viscosity characteristics are critical for worldwide operational capability. Considering that commercial airliners can have a hydraulic fluid capacity exceeding 650 l, it is readily understood why, as more weight requires more fuel, aviation phosphate ester fluids tend to be based on trialkyl phosphate chemistry.

One of the main problems with phosphate ester-based hydraulic fluids is the formation of acids through hydrolysis of the phosphate ester as follows:

$$(RO)_3P{=}O + H_2O \longrightarrow (RO)_{3-x}\overset{O}{\overset{\|}{P}}(OH)_x + x\,ROH$$

The ultimate solution is to keep the fluid dry although this is extremely difficult because of the hygroscopic nature of the fluid which means it readily absorbs moisture from the atmosphere. The only realistic solution is therefore the use of an additive to control the acid formation. Epoxides have been found to be effective in controlling fluid acidity by converting the acidic phosphate esters produced by hydrolysis into a neutral phosphate ester [28].

Another mechanism for the formation of acids is through thermal degradation. There is no easy solution to this problem, so the operational temperatures of the commercial aircraft hydraulic systems must be maintained well below the thermal degradation temperatures of the phosphate ester hydraulic fluids, reported as being above 200°C [26].

Another problem that has been encountered with these fluids in the past is electrochemical erosion of servo valves within hydraulic systems. The rapid flow of the fluid through the valve can cause an electric current to flow between the valve wall and the fluid, thus causing the valve to erode.

Aviation phosphate ester hydraulic fluids are classified into ‘types’ by SAE specification AS1241 [29], with Type I being the earliest fluids and each iteration attempting to improve on one or other of the above performance criteria. Type IV fluids with improved stability and lower density are now commonplace and Type V fluids with still better performance characteristics are now available.

It is important to note that hydrocarbon-based fluids and phosphate ester-based fluids are not interchangeable as the materials that they may contact, e.g. seals, wiring insulation and paint must be carefully selected for whichever hydraulic fluid class is being used on the aircraft. Also, the two different types of fluid must never be mixed.

11.5 Aircraft Greases

There are many components on an aircraft that require lubrication where it is impractical to use liquid lubricants, for instance, spoilers, ailerons, rudders, undercarriage, doors and certain engine components. Greases are used extensively in aircraft applications, particularly for the lubrication of airframe components.

A grease is essentially a lubricating oil with a filler material to hold it in place, but there is much more to the formulation and selection of a grease for a particular application. An airframe grease must perform under a wide variety of conditions, for example, operating temperatures can range from 65°C on the ground in the Middle East to –70°C at 36,000 feet and above. Air pressure at altitude can be as low as 3.3 psi [30]. During service use, grease is exposed to water and, in ice and snow conditions, both aircraft and runway de-icer fluids and it must maintain a satisfactory degree of performance under all of these conditions.

In aircraft wheel bearings grease also has to withstand high-temperature conditions. The wheel brakes, which are in close proximity to the wheel bearings, can reach temperatures up to 550°C and it is important that the grease does not melt and run into the brake material reducing brake efficiency and possibly causing a fire.

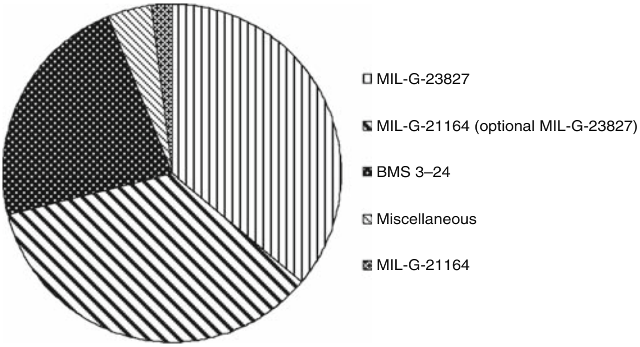
One reason for a grease to lose its consistency when subject to high temperatures is melting of the filler, the grease then becomes liquid and can run out of the application. In respect of the filler used, airframe and wheel bearing greases tend to divide into one of two types, either lithium soap/complex based and clay based. Each has its advantages and disadvantages, one advantage of clay-based greases is that the clay filler does not melt. This is one reason why clay-based greases have been traditionally used for high-temperature applications such as aircraft wheel bearings. However, water ingress can be a problem in a number of applications and modern lithium soap/complex-based greases tend to have better corrosion inhibiting properties while still having good high-temperature capability. Some of the specifications that define modern lithium complex greases include tests to demonstrate that key properties of the grease are not degraded to an unacceptable degree when contaminated with water.

In the past, several grades of grease with different chemical and physical properties have been selected to cover various different applications on aircraft but this presents potential problems. The operator has to purchase several different greases and then ensure that the correct greases are used for the correct applications and that they are not accidentally intermixed. Mixing different grades of grease can lead to degradation of the mixture to the extent that the resulting properties of the mixture are outside those of the two individual greases. In particular the mixing of greases of different filler types is considered undesirable. Incompatibility is most commonly shown by either hardening or softening of the mixture. Consistency, or stiffness, is one of the most important properties of a grease and affects its ability to remain in situ and lubricate effectively, therefore such a situation is to be avoided.

In much the same way as oils are graded by their viscosity characteristics, greases are classified by their consistency characteristics through the NLGI (National Lubricating Grease Institute) classification. The class most commonly used as an airframe grease is NLGI 2 which allows a consistency range, as measured by method IP 50 worked cone penetration [31], of between 265 and 295 mm^{-1}.

One of the simplest ways to reduce the possibility of inadvertent grease intermixing is to reduce the number of different greases required on an aircraft. Much effort has been given recently by the aviation grease community to develop a general-purpose NLGI 2 airframe grease with a filler based on lithium chemistry and PAO/ester base oil. One of the main reasons for choosing lithium chemistry is, as stated earlier, its ability to cope with water contamination. The intended operating temperature range of this grease is –73 to 121°C. One of the main drivers behind this approach has been Boeing with the development of their BMS 3-33 'Grease, Aircraft General Purpose, Low Temperature' specification, in response to airline operator requests to reduce the number of grease types used for routine lubrication. Other major aims were to improve grease performance properties and improve corrosion protection [32]. The two pie charts below show the impact of introducing this new grade of grease into service on the number of greases required for the Boeing 757, Fig. 11.7. These clearly illustrate the logistic advantage of such a general-purpose grease. Further development of this grade of grease was co-ordinated with other OEMs, such as Airbus, military specification authorities such as the UK MoD and grease manufacturers through the SAE Aviation Greases Committee AMS M. The aim was to maximise the commonality of requirements and therefore reduce

757 Grease Recommendations Before BMS 3–33 Introduction (Data provided by Boeing)



757 Grease Recommendations After BMS 3–33 Developed (Data provided by Boeing)

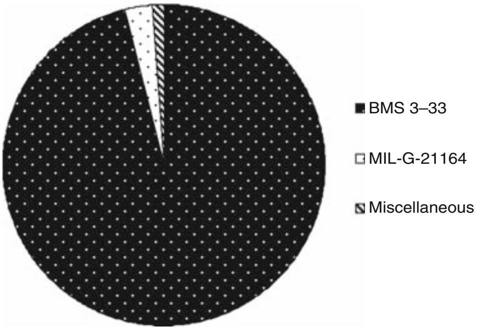


Fig. 11.7 Reduction in grease types following introduction of type BMS 3-33 on Boeing 757

the proliferation of grades used across the aviation industry as much as possible; the result was SAE specification, AMS 3052 [33].

One area where this grease is not expected to be used is in aircraft wheel bearings because of the higher operating temperatures involved. As previously stated, brake temperatures can reach 550°C and are in close proximity to the wheel bearings. The loads are 440–660 psi nominal but could be as high as 1177 psi, with acceleration from 0 to 250 knots in less than 1 s. These bearings are generally only changed when tyres are changed, with tyre life in the region of 200–300 landings. With the development of better greases the target for grease life is 750 landings. Again, the grease must cope with contamination with water and de-icing fluids while maintaining its integrity and protecting the bearings from corrosion.

Much the same logic as was applied to the airframe grease is being applied to the development of a grade of grease specifically aimed at aircraft wheel bearings, NLGI 2. The formulation has lithium chemistry with a PAO/ester base oil but the operating temperature range is shifted upwards to –54 to 175°C, with a dropping point requirement of 250°C minimum. Again this work is being co-ordinated through SAE committee AMS M to ensure as much commonality across the industry as possible. Having both the airframe and wheel bearing greases based on lithium chemistry will also further help to avoid the potential for the intermixing of lithium- and clay-based greases.

11.6 Helicopter Transmission Lubricants

Helicopter transmissions involve a variety of gears, many of them high-speed or highly loaded. They are the most critical gears in aviation because they carry the whole of the power for both thrust and lift and are almost always unduplicated. A further factor to consider is that while helicopters can continue to fly with total engine failure in a controlled glide to ground, if there is a failure of any of the gearboxes, the helicopter is almost bound to suffer an uncontrolled landing. Their proper lubrication is therefore vitally important; there have been serious helicopter crashes in which lubricant failure played a significant part.

The tail rotor gearbox is critical to directional control and stability but carries only about 5% of the total power. It may be lubricated with the same oil as the main gearbox but, because the bearings and gears are relatively small with low linear sliding speeds, they may be grease lubricated.

The most important part of the transmission is the main gearbox, which contains the most heavily loaded reduction gears transmitting power to the main rotor blades. It is always oil lubricated but a variety of different oils are used in different helicopters.

Mineral oils containing extreme pressure additives are used in some helicopters but increasingly, particularly in gas turbine-powered helicopters, ester-based lubricants are used. This may be the same grade of lubricant as used in the engine, or a different grade of engine lubricant, or a grade intended specifically for helicopter transmissions. One such transmission lubricant is a legacy of early supersonic aircraft development, somewhat ironic considering that most helicopters cannot exceed a speed of 200 mph. This occurs because the engines developed for aircraft such as Concorde and the RAF's Tornado required higher load-carrying properties than were offered by the 5 cSt gas turbine lubricants available at that time. That higher load-carrying capability also provides good performance as a helicopter transmission lubricant. In fact some of the brands of lubricant approved under UK engine lubricant specification Def Stan 91-100 are also approved under the US Navy's helicopter transmission lubricant specification DOD-PRF-85734 [34].

Although widely used as such, turbine lubricants were not considered ideal as transmission lubricants [35]. Therefore in the 1970s the UK MoD sponsored a work programme involving GKN Westland Helicopters and Imperial College, with the support of several lubricant manufacturers, to develop a lubricant specifically for helicopter transmissions. The result was a grade of lubricant designed around a 9 cSt ester base oil. One reason for choosing an ester basestock was so that if it was inadvertently put in the engine there would at least be a similarity of chemistry with the ester-based engine lubricant, thus minimising damage through chemical and material incompatibilities.

One property where many helicopter transmission lubricants are weak is corrosion inhibition. One of the reasons is, as stated in Section 11.3.5, that corrosion inhibitors and anti-wear/load-carrying additives can compete for the metal surface to the detriment of each other. One advantage of the thicker 9 cSt base oil is that it can give better EHD lubrication reducing the dependency on load-carrying additives and therefore a rust inhibitor can be used to improve rust inhibition. A cost–benefit analysis predicted that the introduction of this lubricant into a large fleet of aircraft could accrue savings of several million dollars per annum. This grade of lubricant is still under evaluation by specification authorities and helicopter manufacturers and has yet to see service.

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Dedication S. Lee dedicates the turbine lubricants section of this chapter to his former colleague and mentor, John Hughes, who was a major contributor to the development of turbine lubricant specifications in the UK and a key player in the development of SAE specification AS5780.

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Chapter 12
Liquid Lubricants for Spacecraft Applications

S. Gill and A. Rowntree

Abstract Liquid lubricants used for spacecraft have advantages over solid lubricants but there are also disadvantages to consider. The challenge is to ensure that the liquid lubricant does not disappear from the mechanism by evaporation or creep. Lubricants can be used as fluids or formulated as greases. The liquids can be highly refined hydrocarbons, PAOs, silicones, polyol esters (POEs), multiply alkylated cycloparaffins, (MACs) or various perfluoropolyethers (PFPEs). Greases are made from these liquids using thickeners such as lithium, calcium or sodium soaps, PTFE, graphite or lead. Operational temperatures range from –45°C to over 100°C. Low vapour pressures are crucial, below 10^{-8} mbar at 20°C and total weight loss must be <1% for general applications, <0.1% for optical applications. 'Surface creep rates' must be low, temperature gradients and surface R_a are important factors. The wear rates for standard tests using different lubricants vary over several orders of magnitude for different lubricants, surface coatings and rpm. Unexpected effects, such as PTFE 'plating out' at low rpm, occur. The main issues are to prevent the lubricant escaping from working areas and to protect it from degradation by chemical reactions or radiation.

12.1 Introduction

Liquid lubricants have been used in spacecraft mechanisms since the earliest satellites were launched. The vast previous experience gained in terrestrial applications with liquid lubricants means that they were the obvious choice in the early applications and they remain in widespread use today. Some of the advantages of liquid lubrication for aerospace applications, whether by oil or grease, are as follows:

- they are perceived to be simple to apply,
- there are no limitations of the use of lubricant in air/ground operations,
- at medium to high speeds the existence of a fully separating oil film between loaded surfaces in relative motion will provide a very long service life,
- the torque variations, or torque 'noise', are usually smaller with oil than with a dry lubricant, particularly in oscillating or slowly rotating systems,
- the thermal conductance of an oil film is higher than that of a dry lubricant and may be important in some applications.

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However, there are disadvantages and these include the following:

- the variable torque of a bearing system, or efficiency of a geared system, due to the effect of the large temperature variations usually found on the lubricant viscosity,
- due to the small amounts of lubricant used, there is a critical requirement to avoid lubricant loss by creep, evaporation, absorption by porous materials, such as phenolic cages, and any long-term chemical reactivity between lubricant and substrate,
- difficulty in justifying that accelerated testing with fluid lubricated components is fully valid,
- liquid lubricants contaminate nearby surfaces or, in turn, are contaminated by the ingress of debris.

A major challenge with liquid lubricants in space is to ensure that the lubricant does not disappear from the working area, either by creep or evaporation, and that operation in a vacuum does not cause changes which cause the oil to lose its function as a lubricant.

This chapter will first discuss the different generic types of oils and greases used in space lubrication, followed by their important specifications. The performance and some of the limitations of these oils and greases will then be reviewed.

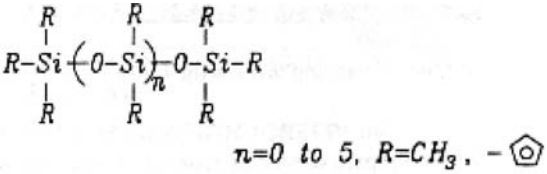
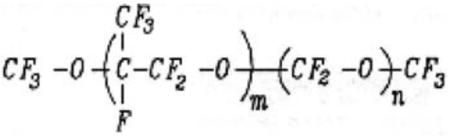
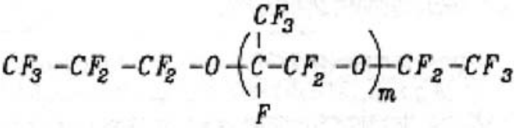
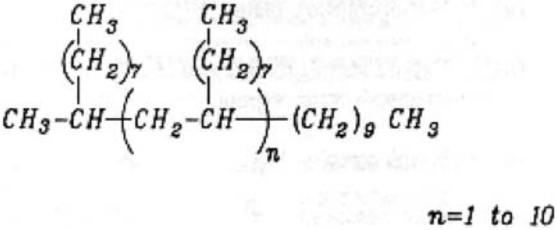
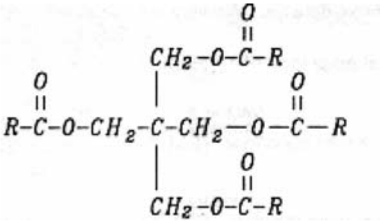
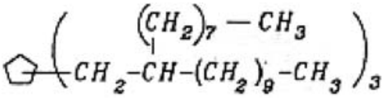
12.2 Types of Liquid Lubricants

12.2.1 Introduction

Historically, many different liquid lubricants have been used in space and this section will give their broad classifications together with examples. The general properties of each type of lubricant will be discussed, trade names given and their current usage analysed. It is worth noting, however, that current usage is usually based around two main classes. Table 12.1 shows the chemical structures of the types of oils that will be discussed. The lists provided are by no means meant to be exhaustive but they do emphasise the dominant lubricant structures used. The situation for the user is complicated still further by the fact that different companies have their own names for similar products and also some product names have changed over the years.

Most of the oils can also be formulated as greases by the addition of thickening agents to make a semi-solid. The thickener is often chosen to possess lubricating properties of its own. Types of thickener include soaps, metallic elements such as lithium, calcium or sodium reacted with a fat or fatty acid, and other additives like PTFE, graphite or lead. Like the parent oils, other additives are often added to greases to provide anti-oxidation properties or improved load-carrying ability. Greases can ensure that the oil remains in its original location for longer periods,

Table 12.1 Space lubricant molecular structures

Type of fluid	Molecular structure
Silicone	 $R-\overset{R}{\underset{R}{Si}}-(O-\overset{R}{\underset{R}{Si}})_n-O-\overset{R}{\underset{R}{Si}}-R$ $n=0$ to 5, $R=CH_3$, -
PFPE, Fomblin F, Braycote 815Z	$CF_3-O(CF_2-CF_2-O)_m(CF_2-O)_n CF_3$
PFPE, Fomblin Y	 $CF_3-O-(\overset{CF_3}{\underset{F}{C}}-CF_2-O)_m-(CF_2-O)_n-CF_3$
PFPE, Krytox	 $CF_3-CF_2-CF_2-O-(\overset{CF_3}{\underset{F}{C}}-CF_2-O)_m-CF_2-CF_3$
PFPE, Demnum	$CF_3-CF_2-CF_2-O(CF_2-CF_2-CF_2-O)_m CF_2-CF_3$
Polyalphaolefin (PAO)	 $CH_3-\overset{\overset{CH_3}{(CH_2)_7}}{CH}-(CH_2-\overset{\overset{CH_3}{(CH_2)_7}}{CH})_n-(CH_2)_9 CH_3$ $n=1$ to 10
Polyolester (POE)	 $R-\overset{O}{\overset{\parallel}{C}}-O-CH_2-\overset{CH_2-O-\overset{O}{\overset{\parallel}{C}}-R}{\underset{CH_2-O-\overset{O}{\overset{\parallel}{C}}-R}{C}}-CH_2-O-\overset{O}{\overset{\parallel}{C}}-R$
Multiply alkylated cyclopentanes (MACs)	

and in some circumstances the thickener can act as a sponge to supply the oil to the loaded zone as required. In addition, greases are often more tolerant of wear debris than the base oil alone.

12.2.2 Mineral (Hydrocarbon) Oils

The extensive use of hydrocarbon oils as lubricants in terrestrial applications has resulted in a good understanding of their properties. They are inherently good boundary lubricants and additives are readily soluble in them. In general, however, they do not have a low vapour pressure, and so their use in space is usually limited to sealed lubricant systems. The oils used in space tend to be super-refined and, as such, they have had all of the light fractions of oil and impurities removed, Table 12.2.

Table 12.2 Commercial mineral hydrocarbon lubricants

Vackote	Ball Brothers, USA	Family of oils
Apiezon	Ball Brothers, USA	Family of oils and greases with many variants
Teresso	Humble Oil, USA	V78 base, V79 with additives
Coray 55	Oil from Exxon, USA	
Andok C		Channelling grease with sodium soap thickener, derived from Coray 55
KG80*	Kendal Refining Co, USA	Oil with anti-oxidant and boundary lubricant additives (TCP – tricresylphosphate)
SRG60*	Kendal Refining Co, USA	From a family of oils with TCP additive
BP110*	British Petroleum	Highly refined hydrocarbon with rust preventative
BP2110*	British Petroleum	Grease from BP110 with oleophilic lead–graphite filler

*No longer in production, though equivalents may be available

12.2.3 Synthetic Oils

The composition of synthetic oils can be carefully chosen to give a desired performance. As would be expected there are many types of synthetic oil and only the most common types used (or proposed for use) in space will be discussed here.

Synthesised Hydrocarbon Fluids or Polyalphaolefins, PAO: Polyalphaolefins are chemically similar to mineral oils, the latter being random mixtures of hydrocarbons whereas the difference for polyalphaolefins is that their composition is carefully chosen and controlled. Their vapour pressures are generally lower than mineral oils and, like mineral oils, they can be readily blended with conventional additives to provide wear, oxidation and corrosion protection. A typical polyalphaolefin is Nye 179, one of a family of PAOs covering a wide viscosity range.

Silicones: The silicone fluids are polymers based on the dimethylsiloxane structural unit. Their properties are varied according to the extent of polymerisation, i.e.

molecular weight, which can be tailored to offer many of the properties a space lubricant requires, such as:

- high viscosity index,
- low pour point,
- low vapour pressure.

In the early years of space exploration silicones were therefore often used. However experience has shown that their low surface tension means that they tend to creep out of the contact zones. Also, they degrade and produce polymer deposits in contact zones. Silicone fluids are therefore no longer considered as suitable space lubricants, but they are still used as damper fluids or for thermal conduction. Typical commercial silicone fluids used in aerospace are given in Table 12.3.

Table 12.3 Examples of typical silicone fluid lubricants used in aerospace

Versilube F50	Manufactured by General Electric, USA	No additives
Versilube F44	Do	Anti-oxidant and extreme pressure additives added
Versilube G300	Do	F50 with lithium-based soap

Synthetic Esters; Polyol or Neopentyl Esters, POE or NPE: A group of compounds of which the polyol or neopentyl esters have generated the most interest. They were developed for their wide operating temperature range and low volatility, Table 12.4.

Table 12.4 Synthetic polyol or neopentyl esters used in aerospace

Nye 238		From a family of oils
BP135	BP	Former BP oil (and grease BP8135) developed for turbine engines
PDP-65	Klüber product	

Multiply Alkylated Cyclopentanes, MACs: Multiply alkylated cyclopentanes are a relatively new class of fluids prepared from dicyclopentadiene by reaction with aliphatic alcohols. Typical examples of commercial MAC fluids are shown in Table 12.5. The properties of this class of fluid are tailored by varying the nature of the alcohol in the synthesis. Vast ranges have been achieved. These fluids readily absorb additives. Pennzane SHF-X2000 has been under intensive investigation and is now widely used in spacecraft mechanisms.

Table 12.5 Multiply alkylated cycloparaffins used in aerospace

Pennzane SHF X2000	Pennzoil, USA
Rheolube 2000	Nye grease with anti-oxidant and anti-wear additives

Perfluorinated Lubricants, PFPE: The full name of this class of fluids is the perfluoroalkylpolyethers, hence the acronym PFPE. They are a family of fluids formulated as long-chain linear polymers built up from carbon, oxygen and fluorine atoms. The fluorine polymer structure makes them chemically inert and stable over a wide temperature range. The disadvantage is that they will not usually dissolve standard additives, although soluble additives have been developed for them. This type of lubricant has been the one most used in spacecraft mechanisms in recent years. There is a vast range of trade names for this type of oil/grease, some of the more prevalent ones are given in Table 12.6.

Table 12.6 Commercial examples of perfluoroalkylpolyether fluids used in aerospace

Fomblin YVAC	Group of Y-type fluids made by Montedison/Enimont
Fomblin Z25	Specific oil of Z-type made by Montedison/Enimont
Fomblin ZNF	Grease based on Z25 with 27% PTFE
Brayco 815Z	Similar to Z25, produced by Castrol Speciality Products, USA
Braycote 601	Grease made from 815Z with PTFE thickener and rust inhibitor
Demnum	Range of oils made by Daikin Industries, Japan
Krytox	Range of oils and greases made by Du Pont, USA
Barrierta	Klüber produced range, based on Tyreno fluids
Maplub PF 100	Similar to Braycote 601
Maplub PF 101	Similar to Braycote 602 (i.e. +MoS_2)

Silahydrocarbons: This class of lubricants contains only silicon, carbon and hydrogen and are based on the number of silicon atoms present in the molecule (tri, tetra or penta). They exhibit very low volatility. They have been recently developed and initial research suggests good performance compared with PFPEs or MACs. They should not be confused with the silicone fluids.

12.3 Specifications

12.3.1 Temperature Range of Operation

Aerospace lubricants are frequently required to operate over a wide temperature range, often from around −45°C to in excess of +100°C. They must not degrade at the maximum temperatures anticipated to occur in storage, launch and service conditions.

As viscosity increases with decreasing temperature, another very important property of the oil is therefore the 'pour point'. This gives an approximate indication of the lowest temperature at which it is usable, depending on the maximum viscosity that can be tolerated in each application. The general principle is not to operate within ~10°C of an oil's pour point and also to expect large rises in torque below

0°C as viscosity increases. Figure 12.1 shows the effect of temperature on the torque of an air conditioning bearing pair, as a function of lubricant type on the mean frictional torque (the lubricants are described in Table 12.7).

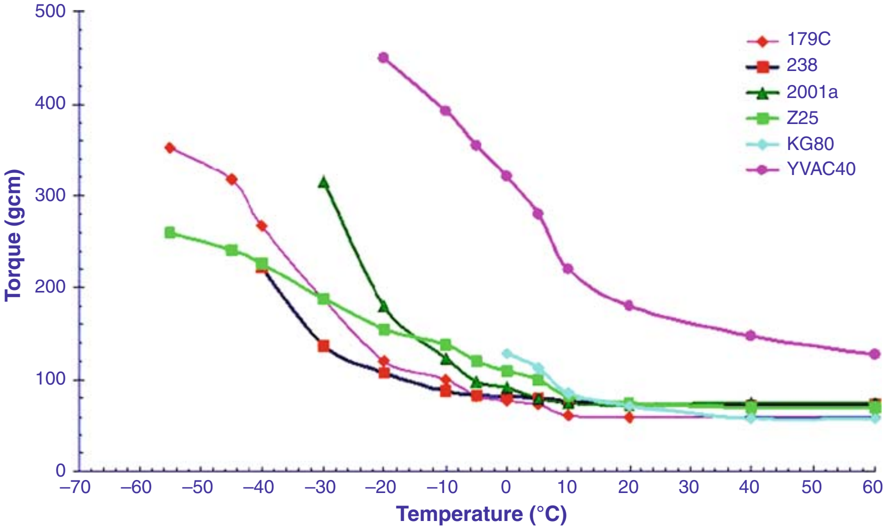


Fig. 12.1 Effect of temperature on mean torque of an air conditioning bearing pair, as a function of lubricant type

12.3.2 Vapour Pressure

The vapour pressure of an oil, and any additives it may contain, is an essential parameter to consider. Vapour pressure is defined as the pressure that the oil would exert in a closed system if it alone were present, under conditions where the liquid and gaseous phases are in equilibrium at a known temperature. The vapour pressure varies non-linearly with temperature, and for many oils it is not unusual for it to increase by a factor of up to 10^4 or 10^5 between 20 and 100°C. The vapour pressure of an oil is usually quoted as the value at +20°C. For those substances which have a low vapour pressure, $<10^{-5}$ mbar, at +20°C this property is usually measured at elevated temperatures and the value at +20°C is evaluated by extrapolation.

It is normal practice with mechanisms that are exposed to the vacuum of space to avoid using oils that have a vapour pressure at 20°C higher than about 10^{-8} mbar. In completely enclosed systems, however, such as momentum wheel bearings, operating in a partial vacuum, it may be possible to tolerate oil having a vapour pressure as high as 10^{-6} mbar.

12.3.3 VCM Properties

The weight loss of a lubricant which will occur due to evaporation in vacuum, and how much contaminating material could condense on to a nearby cooler surface is also important. This outgassing will be time and temperature dependent. The outgassing rate is measured in a standardised NASA or ESA MICRO-VCM screening test, where the percentage total mass loss, TML %, of a heated sample in vacuum is found, together with the collected volatile contaminant material, CVCM %, which condenses on a cooled plate of standard dimensions. There are two sets of acceptable limits for material outgassing:

Group A:	General spacecraft applications	TML% < 1.0% CVCM < 0.1%
Group B:	Optical device applications	TML% < 0.1% CVCM < 0.01%

The limits quoted above can be made more stringent if the materials are to be used in very critical areas. If required, the collector plate can be examined by an infrared spectrometer to determine the IR spectrum, and hence chemical nature, of the contaminants. The use of materials deemed acceptable by these limits does not necessarily ensure that contamination will not occur. The screening test is done at 125°C in order to accelerate the outgassing to ensure a measurable change is observed. Comparisons of various materials are thus only really valid at this temperature. The measurement of contamination is only comparative and also strictly valid for collectors at 25°C with similar surface adhesion properties. Also it is worth noting that this test says nothing about the species that is being evaporated.

12.3.4 Creep Rate

'Surface creep' must be very low, both to restrict loss of lubricant from bearings, etc. and to avoid contamination of other components. Creep is a surface tension effect where oil surface tensions are typically in the range 18–30 mN/m. To mitigate surface creep, thermal gradients should be avoided or minimised and the surface finish of components should be optimised. Capillary creep occurs if $R_a > 0.1$ mm, thermal creep occurs if $R_a < 0.6$ mm.

12.3.5 Effects of the Space Environment

Little data are available at this time on the tolerance of liquid lubricants to radiation exposure but assessment of this may be important for some future spacecraft. In low earth orbit applications the lubricant is normally within an enclosure and exposure to atomic oxygen, the main environment in this orbit, is not therefore considered to be a problem.

12.3.6 Storage

The lubricant may spend a long period of time in storage before being added to a mechanism component. The completed component or mechanism may itself then spend a second period of storage, perhaps not in ideal conditions, before operation in space is realised. The lubricant must not in any way degrade during this time and should be chemically assessed by the manufacturer if there are any doubts prior to use. Migration due to gravity can also occur if the mechanism is stored in the same orientation for long periods.

12.3.7 Chemical Inertness/Rust Prevention

There must be no adverse chemical reaction with any material that the lubricant may come into contact with during flight, including wear debris. The lubricant must not result in corrosion of, for example, bearing or gear surfaces in vacuum during the lifetime of the mechanism. Thus, it is essential to investigate the corrosion protection afforded not only by the lubricant as supplied but also by any degradation products which may be generated as a result of changes in chemical composition under shear and in the presence of steel wear debris.

12.3.8 Table of Comparative Data

Table 12.7 gives some of the physical specification data relating to some of the oils and greases given as examples in the previous sections.

12.4 Some Limitations of Space Oils

12.4.1 Approximate Lives of PFPEs and Ways of Improvement

Several of the PFPE fluids have been studied in-depth by Stevens, Baxter, Carre, etc. as given in the bibliography to this chapter. Some of the important conclusions are reviewed here, since they impose some limitations on the use of PFPE oils and greases in specific applications.

With Z25 and 815Z oils in AISI 52100 steel ball bearings at speeds of 100, 200 and 1400 rpm in vacuum tests, the fluid has been found to degrade by the formation of a black polymeric material on the races and balls after prolonged operation of the order of 10^7–10^8 revolutions. This polymeric material is insoluble in the oil and its presence has the effect of causing some of the remaining free oil to draw away, or ‘de-wet’, from the loaded ball/race contact. This phenomenon, in the presence of steel wear debris, causes a rapid increase in the wear rate, and of course the torque noise, from the bearings and rapidly leads to failure. The solid polymer has been confirmed to be a perfluoro-polymer. Although there are conflicting theories to explain this chemical and physical degradation, when the bearing surface is worn

Table 12.7 Summary of space oil properties

Name	Type	Viscosity at 20°C (cSt)	VI	Pour point (°C)	Vapour pressure mbar at 20°C	VCM TML (%)	VCM RML, 5%	Density	Mol. Wt.
Vackote	Mineral oil	210	108	–41	$1 \times E^{-08}$			0.88	574
Apiezon C	”	283	110	–12	$1 \times E^{-08}$			0.88	479
Terroso V78	”	400	105	–7		31.5		0.84	
Coray 55	”	220	98	–15	$1 \times E^{-05}$				
Andok C	Grease	220	98	–15	$1 \times E^{-05}$	40			
KG80	Mineral oil	340	109	–10	$1 \times E^{-08}$	41	41	0.87	
SRG60	”	108	105	–10	$1 \times E^{-06}$			0.87	
BP110	”	300	107	–24	$3.7 \times E^{-08}$	22.5	25.5	0.87	700
BP2110	Grease	300	107	–24	$4.0 \times E^{-08}$	17.5	17.5		700
NYE 179	PAO	66	139	–60				0.83	
Versilube F50	Silicone	100	130	–70					1.05
Versilube G300	Grease	100	130	–73	$1 \times E^{-07}$	5.7			
NYE 238	Synthetic ester	55		–62				0.94	
BP 135	”	70	137	–57	$1 \times E^{-08}$			0.96	520
PDP-65	”	135	280	–45	$7.6 \times E^{-08}$	80	80	0.91	
NYE Oil 2001A	MAC	260	137	–45	$4 \times E^{-11}$			0.85	910
Rheolube 2000	Grease	260	137	–45	$1.3 \times E^{-11}$				
Fomblin	PFPE	460	135	–32	$9 \times E^{-12}$	0.07	0.06	1.91	3900
YVAC40	”	260	358	–75	$1.6 \times E^{-13}$	0.04	0.03	1.85	9500
Fomblin Z25	Grease	260	358	–70	$2 \times E^{-12}$				
Fomblin ZNF	PFPE	250	350	–73	$2 \times E^{-12}$	0.03	0.02	1.87	10,000
Brayco 815Z	”	250	350	–73	$5 \times E^{-12}$	0.14	0.13		
Braycote	Grease	500	210	–53	$5 \times E^{-11}$			1.89	8400
Demnum S-200	PFPE	800	134	–35	$1 \times E^{-06}$	2.28	2.28	1.9	6250
Krytox 143AC Barrierta	”	280	120	–50	$1 \times E^{-09}$	15.6	15.5	1.95	3500

the lubricant reacts with the active steel surface resulting in a buildup of wear debris and polymer deposits. It has been proposed that the formation of ferric fluoride on the steel surface finally results in a complete catalytic degradation of the oil.

There is limited experimental work to suggest that the use of 440C stainless steel bearings may ensure a longer lifetime from Z25 than 52100 bearing steel. Tests have also shown that the useful life of Z25 can be much further extended, by a factor of at least ×10, in SAE 52100 bearings with TiC ceramic-coated 440C stainless steel balls, thereby preventing the lubricant reacting with ferritic wear debris. Thin films of lead have also been found to confirm increased degradation and corrosion resistance with PFPE lubricants. A summary of some typical test results is given in Fig. 12.2.

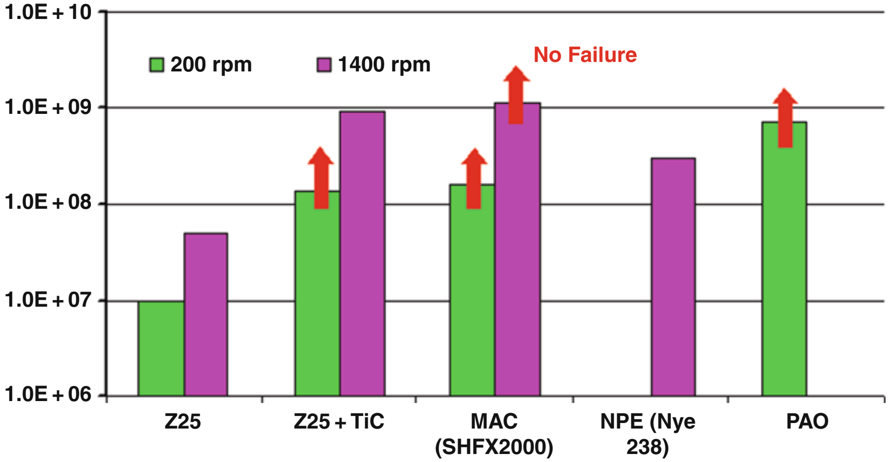


Fig. 12.2 Comparative life of differing lubricants in air conditioning ball bearings

12.4.2 *Effect of PTFE Filler on Bearing Torque*

PTFE ‘plate-out’ can occur in low-speed greased bearings, with serious increases in bearing torque, as shown in Fig. 12.3.

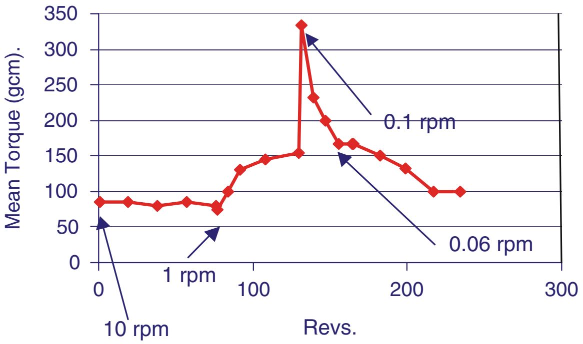


Fig. 12.3 Effect of speed on torque of PTFE grease-lubricated air conditioning ball bearings

12.4.3 Testing and Acceleration Factors

Testing of liquid lubricants, especially for long-term applications, is a major problem that can lead to erroneous conclusions if care is not taken. Acceleration factors should be chosen with very great care since they influence the lubrication regime in which the component is operating and can thus influence their effective behaviour. In addition, short-term testing, for instance, by cutting out nascent periods in the operation, accurately simulates the motion requirements but does not reflect the true evaporative losses of oils, or the incorporated additives, and this too can lead to over-optimistic conclusions.

12.5 Conclusions

Oils and greases provide a relatively simple means of lubrication in spacecraft applications. They can give low torque variation and good thermal transfer properties when correctly specified. There are some fundamental problems with operation in vacuum and zero gravity, however, which should always be borne in mind.

The major tasks are to ensure that the liquids do not escape from the working areas, either by creep or evaporation, and to ensure that the lubricant is not degraded by any chemical reactions. Additives may be incorporated to improve the performance of oils and greases; however, their vapour pressure and solubility must also be carefully considered.

Oils and greases will evaporate throughout their operational lives, and care must be taken to ensure that there is always sufficient lubricant and also that the vapour does not have a deleterious effect on other spacecraft components.

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Chapter 13
Marine Lubricants

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Abstract Marine diesel engines are classified by speed, either large (medium speed) or very large (slow speed) with high efficiencies and burning low-quality fuel. Slow-speed engines, up to 200 rpm, are two-stroke with separate combustion chamber and sump connected by a crosshead, with trunk and system oil lubricants for each. Medium-speed diesels, 300–1500 rpm, are of conventional automotive design with one lubricant. Slow-speed engines use heavy fuel oil of much lower quality than conventional diesel with problems of deposit cleanliness, acidity production and oxidation. Lubricants are mainly SAE 30/40/50 monogrades using paraffinic basestocks. The main types of additives are detergents/dispersants, antioxidants, corrosion inhibitors, anti-wear/load-carrying/ep, pour-point depressants and anti-foam compounds. There are no simple systems for classifying marine lubricants, as for automotive, because of the wide range of engine design, ratings and service applications they serve. There are no standard tests; lubricant suppliers use their own tests or the Bolnes 3DNL, with final proof from field tests. Frequent lubricant analyses safeguard engines and require standard sampling procedures before determination of density, viscosity, flash point, insolubles, base number, water and wear metal content.

13.1 Introduction

The lubrication of marine diesel engines presents its own particular problems, arising from the sheer size of these engines, their high efficiencies and the fuel they burn. Cylinder bore diameters can be in excess of 1 m and their high efficiency is achieved with firing pressures of 150 bar, resulting in liner temperatures of over 200°C. The fuels burned include poor-quality residual fuels with viscosities of 100 cSt at 80°C, sulphur contents of 4% or more and carbon residues of up to 22% wt. In addition, the crankcase oil charge is simply topped up and only drained if excessively contaminated.

Until the 1990s, any discussion concerning the lubrication of marine engines would have included steam turbines but, due to the rapid escalation of fuel prices in the late 1970s, their use has been virtually discontinued. The improved design and

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efficiency of modern marine diesel engines means that steam turbines are no longer used even for cruise vessels or large, 250,000 tonne, crude oil carriers [1].

Marine lubrication includes the use of ancillary products such as hydraulic oils, compressor oils, gear oils and grease; these applications are discussed in Chapters 8 and 14. A sound knowledge of these and other lubricants is required for those concerned with marine lubrication. Suppliers of marine lubricants are faced with considerations not always applicable to other lubricating oils. Any given marine lubricant must be available at the same quality, at relatively short notice and at literally hundreds of ports throughout the world. In addition, the ship operator frequently requires advice on lubrication and related problems, together with a used oil sample analysis service.

13.2 Marine Diesel Engines

13.2.1 Classification by Engine Speed

Diesel engines are classified by their rpm, as shown in Table 13.1. The majority of marine propulsion engines are slow-speed, two-stroke engines and the remainder are mainly medium-speed engines. The principal characteristics of the two engine types are outlined in the following sections.

Table 13.1 Classification of diesel engines by speed

Type	Speed (rpm)	Bore (mm)	Output (kW/cyl)
Slow speed	60–200	300–1050	560–4900
Medium speed	300–1000	300–700	75–1500
Medium/high speed	600–1500	200–400	75–225
High speed	600–2000	100–200	15–150

13.2.2 Slow-Speed Engines

Most slow-speed diesel engines run at speeds in the range 60–120 rpm and operate on high viscosity residual fuel oil. Propeller efficiency is proportional to engine speed and their low speed enables these engines to be coupled directly to the propeller shaft without the use of a gearbox, aiding mechanical efficiency. Slow-speed diesel engines are frequently referred to as ‘crosshead engines’ because of their construction. For each cylinder, the piston rod and connecting rod are linked to a reciprocating block, the crosshead, which usually slides up and down in guides. The crosshead separates the firing cylinder from the crankcase and a stuffing box completes the seal. The cylinders and crankcases are lubricated separately by cylinder and system oils, respectively.

The cylinder oil is fed to the cylinder walls through a number of injection points, called quills. Each cylinder can be fitted with between 4 and 16 quills, depending upon the cylinder stroke and bore. The quills are arranged circumferentially at either one or two levels and the oil is delivered to them by pumps which may be hydraulically or engine driven.

The system oil is used for forced lubrication of the various bearings and crosshead guides present in the crankcase. In some engines it is also used for cooling the piston undercrowns.

13.2.3 Medium-Speed Engines

Medium-speed engines may be defined as trunk piston engines having a rated speed of between 300 and 1000 rpm. In contrast to the slow-speed engines, the connecting rod is attached directly to the piston gudgeon pin, similar in design to normal automotive diesel engines but on a considerably larger scale. Most are designed to operate on blended heavy fuel oil. As propulsion units, these engines are coupled to the propeller shaft through a gearbox because of their higher speed. Auxiliary engines, e.g. engines used to provide electrical power when the ship is in port, are normally medium-speed engines.

A single lubricant is used for crankcase and cylinder lubrication in trunk piston engines. All major moving parts of the engine, i.e. main and big end bearings, camshaft and valve gear, are lubricated by a pumped circulation system. The cylinder liners are lubricated partially by splash lubrication and partially by oil from the circulation system which finds its way to the cylinder wall through holes in the piston skirt via the connecting rod and gudgeon pin. A recent trend is for medium-speed engines to have cylinder lubrication – as in slow-speed engines – with the excess returning directly to the crankcase.

Another recent trend has been the introduction of a new design of cylinder liner to minimise any tendency to bore polishing. Special rings have been fitted at the top of the liner which effectively scrape away most ring face deposits that might rub against the liner. One consequence of this new design is a dramatic reduction in lubricant consumption. This, in turn, means that the lubricant must be designed to perform over a longer period of service. This is reinforced by another trend towards relatively smaller sump and oil charge volumes. Figure 13.1 is a simplified diagram illustrating the design features of the crosshead and trunk piston engines. The diagram also indicates the relative size of the two types of engine. Typical characteristics of a selection of crosshead and trunk piston engines are given in Tables 13.2 and 13.3, respectively. The different types find typical applications, as shown in Table 13.4. Figure 13.2 shows the size of a modern crosshead engine.

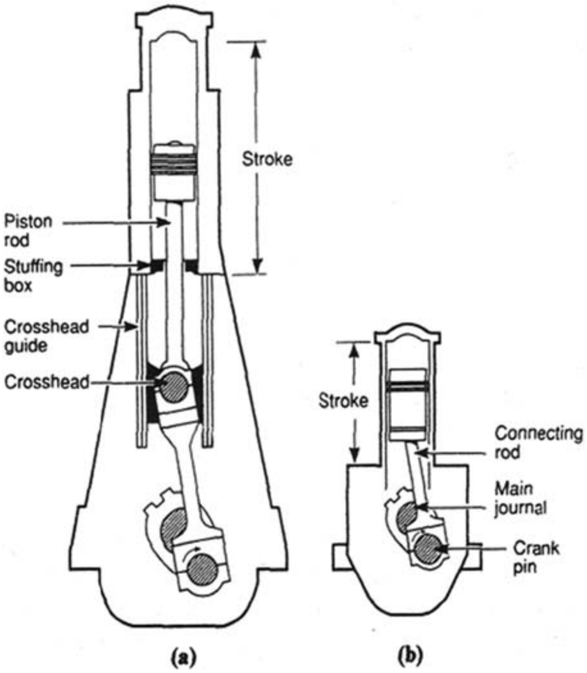

Fig. 13.1 Simplified comparison of (**a**) crosshead and (**b**) trunk piston engines

Table 13.2 Characteristics of large bore crosshead engines

Manufacturer	MAN B&W	Sulzer	Mitsubishi
Engine type	L90 MC-C	RTA 84T-D	UEL85LSII
Bore (mm)	900	840	850
Stroke (mm)	2916	3150	3150
Stroke:bore ratio	3.24	3.75	3.71
Engine (rpm)	73	76	76
Bmep (bar)	19.0	18.5	17.1
Output (kW/cyl)	4880	4100	3862

Table 13.3 Characteristics of medium-speed trunk piston engines

Manufacturer	MAN B&W	MAK	Pielstick	Sulzer	Wartsila
Engine type	L58/64	M601	PC4-2	ZA40S	46
Bore (mm)	580	580	570	400	460
Stroke (mm)	640	600	630	560	580
Engine (rpm)	428	425	429	510	514
Bmep (bar)	23.0	19.9	21.5	25.1	26.1
Output (kW/cyl)	1390	1210	1215	750	1050

Table 13.4 Typical applications for engine types

Slow speed	Medium speed	Medium/high speed	High speed
Main engines for	Main engines for	Tugs	Small boats
General cargo	Cruise liners	Inland waterways	Pumps
Container vessels	Ro-ro ferries	Trawlers	Auxiliary generators
Bulk carriers	Container vessels	Locomotives	Compressors
Tankers	Electric power generation	Auxiliary power	Small ferries
		Power generation for all ships	

13.3 Fuel Oil

Slow-speed crosshead engines operate on heavy fuel oil, with marine trunk piston engines using a range of fuels from marine diesel to heavy fuel oil [2–4]. Heavy fuel oil contains a complex and variable mixture of refinery distillates and byproducts. These include vacuum distillation and visbroken residues, catalytically cracked bottoms, propane de-asphalted residue, lubricating extracts and slop wax. No standard for marine fuel oil quality existed until the introduction of BS MA100 in 1982 [3]. Fuel was purchased simply on the basis of viscosity and density. Since then, International Standard ISO 8217 (1987) [4] and CIMAC (Conseil International des Machines à Combustion) recommendations (1990) have been published [5]. The current British Standard is BS MA100:1996 [6], identical with ISO 8217:1996, and an extract from Table 13.2 of this standard 'Requirements for marine residual fuels' is given in Table 13.5. These publications do not include any measure of fuel ignition quality because no official method exists. Various procedures have been proposed of which the most successful is probably the Calculated Carbon Aromaticity Index, CCAI [7, 8], based on viscosity and density measurements. Many combustion studies on heavy fuel oil have been reported [9–13].

The quality of marine fuel has a direct impact on engine operation, and fuel quality has deteriorated in recent years with the increased use of secondary refining processes [14]. This deterioration in marine fuel quality is a direct consequence of the drive to maximise the yield of premium products from crude oil which has produced heavier residues with poorer combustion properties and more impurities. Engine design has been continuously improved to combat the poorer combustion properties [15–17]. Improved centrifugal separators and procedures have been introduced to reduce impurities such as water, ash and catalyst fines [18–20]. Improved lubricant design can also help engine performance, e.g. increased detergency/dispersancy to solubilise deposits resulting from poor combustion, increased basicity to neutralise sulphur acids and added antioxidants to improve oxidation stability.

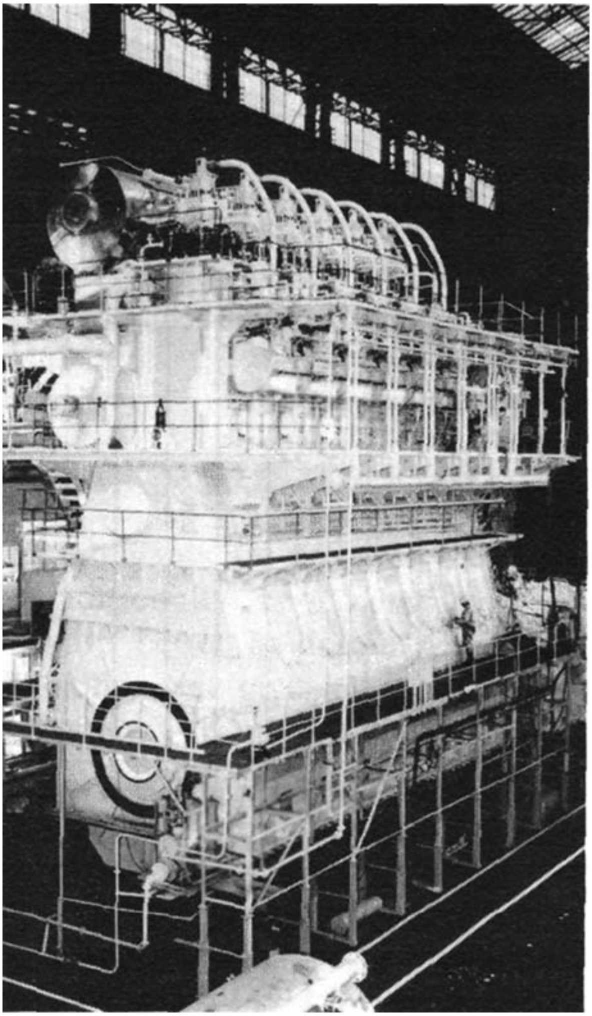

Fig. 13.2 MAN B&W type 6L 90MC slow-speed engine in the builder's shop. Cylinder bore 900 mm, stroke 2916 mm, output 23,460 kW at 78 rpm. Courtesy of MAN B&W Diesel AjS, Copenhagen, Denmark

During the 1990s there was a marked increase in problems arising from complex aromatic asphaltenic species in fuel and their incompatibility in predominantly paraffinic lubricants. This marine 'black paint' phenomenon led to progressively darker and more tenacious surface coatings, especially in rocker boxes and crankcases. Lubricant suppliers resolved this by altering the balance of detergents used in trunk piston oils.

Table 13.5 Requirements for marine residual fuels

		Category ISO-F-										
Characteristic	Limit	RMA 30	RMB 30	RMD 80	RME 180	RMF 180	RMG 380	RMH 380	RMK 380	RMH 700	RMK 700	Test method reference
Density, 15°C, kg/m^3	max	960.0	975.0	980.0	991.0		991.0		1010.0	991.0	1010.0	ISO 3675 or 12185
Kinematic viscosity, 50°C, mm^2/s	max	30.0		80.0	180.0		380.0			700.0		ISO 3104
Flash point, °C	min	60		60	60		60			60		ISO 2719
Pour point (upper), °C												ISO 3016
– Winter quality	max	0	24	30	30		30			30		
– Summer quality	max	6	24	30	30		30			30		
Carbon residue, % (m/m)	max	10		14	15	20	18	22		22		ISO 10370
Ash, % (m/m)	max	0.10		0.10	0.10	0.15	0.15			0.15		ISO 6245
Water, % (v/v)	max	0.5		0.5	0.5		0.5			0.5		ISO 3733
Sulphur, % (m/m)	max	3.50		4.00	4.50		4.50			4.50		ISO 14956 or 8754
Vanadium, mg/kg	max	150		350	200	500	300	600		600		ISO 14957 or 501

Table 13.5 (continued)

		Category ISO-F-										
Characteristic	Limit	RMA 30	RMB 30	RMD 80	RME 180	RMF 180	RMG 380	RMH 380	RMK 380	RMH 700	RMK 700	Test method reference
Total sediment potential, % (m/m)	max	0.10		0.10	0.10		0.10			0.10		ISO 10307-2
Aluminium plus silicon, mg/kg	max	80		80	80		80			80		ISO 10478
Used lubricating oil, ULO		The fuel shall be free of ULO – considered to be free of ULO if one or more of the elements zinc, phosphorus and calcium are below or at the specified limits. All three elements must exceed the same limits before a fuel shall be deemed to contain ULO										
Zinc, mg/kg	–	15										
Phosphorus, mg/kg	–	15										IP 501/IP 470
Calcium, mg/kg	–	30										

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13.4 Base Oils

Most modern marine lubricants are prepared from good-quality paraffinic base oils although, traditionally, naphthenic basestocks were preferred. Paraffinic base oils have better oxidation resistance, a higher viscosity index and lower volatility but give harder carbon deposits. However, modern additive technology can modify the hard deposits allowing paraffinic base oils to be used and thereby making use of their other superior properties.

Marine lubricants are supplied as monograde oils ranging from SAE 20 to SAE 60, with the SAE 30 and 40 grades predominating for trunk piston engine oils and SAE 50 as the main cylinder oil grade, SAE J-300, 1992 [21]. System oils are invariably SAE 30. The complete range of viscosities can be blended from three basestocks which are generally 150 SN, 500 SN and Brightstock. All base oils are screened and approved by the marine lubricant supplier to ensure that the quality of their products is consistent worldwide.

Synthetic lubricants are starting to find limited specialised applications and trunk piston engine oils of 12 and 30 base number (BN) are available. They are currently based on polyalphaolefins with the inclusion of esters to improve additive solubility and seal compatibility.

13.5 Additives

13.5.1 Main Additive Types

Many additives used in marine diesel lubricants are multifunctional and their properties and functions, with particular reference to marine applications, are discussed below. The main types of additives used for formulating marine lubricants are as follows:

- alkaline detergents/dispersants,
- antioxidants,
- corrosion inhibitors,
- anti-wear, load-carrying and extreme pressure additives,
- pour-point depressants,
- anti-foam additives.

13.5.2 Alkaline Detergents

Overbased calcium detergents, with base numbers ranging from 250 to 400, form the backbone of the majority of marine lubricants. Although their principal function is to supply alkalinity to neutralise sulphur acids resulting from the high sulphur fuels, they also contribute detergency. Materials used include calcium sulphonates (natural and synthetic), phenates, salicylates and carboxylates. Except for calcium sulphonates, where all the alkalinity is in the form of micellar calcium carbonate, the alkalinity is built into the detergent molecule itself. Most formulations are based on a balanced blend of two detergent types. Low base detergents, such as calcium sulphonates, with a soap content of approximately 40% and BN (base number) of 5–25, are frequently included to help maintain engine cleanliness and provide additional protection against rust and corrosion.

13.5.3 Dispersants

Ashless dispersants, like detergents, are included to improve engine cleanliness. Most are of the polyisobutylene–succinimide or polyisobutylene–succinate ester type and three basic structures can be identified as mono-succinimides, bis-succinimides and succinate esters. Bis-succinimides are normally used for marine applications because although they are less effective in peptising the low-temperature sludge found in gasoline engines rather than mono-succinimides, they give better diesel engine performance by reducing lacquer formation.

13.5.4 Antioxidants

Both chain-terminating oxidation inhibitors, e.g. hindered phenols and amines, and peroxide-destroying inhibitors, e.g. dithiophosphate and dithiocarbamates, can be included in marine formulations. Mixtures of phenols and amines are often used for synergy but they must have good high-temperature performance. The sulphur-containing oxidation inhibitors also have extremely useful anti-wear properties. Oxidation inhibitors can be used advantageously in some base oils refined from low sulphur crudes and in synthetic basestocks. They compensate for the lack of natural antioxidant species.

13.5.5 Corrosion Inhibitors

Not unexpectedly, marine crankcase oils are sometimes contaminated with water, which is normally removed by the lubricating oil centrifuge. To assist further in protecting against rusting, inhibitors such as alkyl sulphonates, phosphonates, amines and alkyl succinic acids/esters can be added. They work by forming a hydrophobic film on the metal surface but must be selected with due regard to the other additives present.

Non-ferrous metals, although resistant to attack by oxygen and water, can be corroded by acids arising from the products of combustion and oxidation of the lubricating oil. Corrosion can be combated in two ways: neutralisation with low base alkaline earth detergents and the formation of a protective barrier. Oxidation inhibitors can also assist by reducing the formation of acids from oxidation of the lubricant.

13.5.6 Anti-Wear, Load-Carrying and Extreme Pressure Additives

Load-carrying requirements are generally less severe for marine than automotive applications, e.g. there are no specialised cam and tappet test requirements. Nevertheless, good load-carrying properties are required particularly for crankcase oils. The requirements are achieved through the use of compounds such as zinc dithiophosphates, dithiocarbamates, sulphurised fatty esters, disulphides and sulphurised alkenes.

13.5.7 Pour-Point Depressants

The removal of wax in the refining of a base oil is moderately expensive and for this reason paraffinic base oils are normally only produced with pour points of no lower than –12°C. Pour points of this level are not acceptable for many marine applications, e.g. oil used in deck machinery, and pour-point depressants are therefore added, usually in the range 0.1–0.5%. Materials used include polyalkylmethacrylates, alkyl naphthalenes and alkylated wax.

13.5.8 Anti-Foam Additives

Silicone-based oil-insoluble additives are incorporated at extremely low dosage to control any tendency to form stable foam. It is important that they are dispersed throughout the oil and within an appropriate particle size range, achieved using a high-shear stirrer.

13.6 Properties and Formulation of Marine Lubricants

Typical properties of the three types of marine diesel engine lubricants are summarised in Table 13.6. The three types of engine lubricants have quite different performance requirements, summarised in Table 13.7.

There is no simple system for classifying marine engine lubricants comparable to the well-known API system of CD, CE, CF and so on for automotive diesel lubricants because they are used in such a range of designs, ratings and service applications on engines burning a wide range of fuels. Consequently, the lubricants are developed through a series of laboratory, rig and engine tests culminating in

Table 13.6 Typical properties of marine diesel engine lubricants

	System oil	Cylinder oil	Trunk piston engine oil	Test method
Viscosity grade	SAE 30	SAE 50	SAE 40	
Viscosity (cSt) at 40°C	103	218	138	ASTMD445
Viscosity (cSt) at 100°C	11.5	19.0	14.0	ASTMD445
Flash point, closed cup (°C)	225	210–212	220	ASTMD93
BN (mg KOH/g)	5	60–80	15–50	ASTMD 2896
Pour point (°C)	–18	–12	–18	ASTM D97

Table 13.7 Performance requirements of marine diesel engine lubricant

Slow-speed crosshead		Medium-speed trunk piston
System oil	Cylinder oil	Crankcase oil
SAE 50	SAE 40	SAE 40
Good oxidation stability	Neutralise sulphur acids	Prevent ring sticking Control piston deposits
High thermal stability	Prevent scuffing	Neutralise sulphur acids
Keep crankcase clean	Provide film strength	
Release water and insolubles	Remove deposits	Retain alkalinity
Aid load carrying	Improve anti-wear	Protect bearings from corrosion
Low emulsibility	Compatible with system oil	Assist load carrying
Prevent rust and corrosion		

shipboard trials. The results are shared with the engine builder when seeking formal approval.

Tests used in developing the various lubricants are outlined in the next three sections. Many of these tests are used for more than one type of oil.

13.7 System Oils

13.7.1 Introduction

Traditionally, system oils were simply rust- and oxidation-inhibited mineral oils but the use of high sulphur residual fuels required the introduction of alkaline system oils to provide adequate corrosion protection. A typical system oil now has a BN (base number, see Section 13.8.2) of 5 and sufficient detergency to keep crankcases and piston cooling spaces clean. They are also used to lubricate turbo chargers, stern tubes, deck machinery, geared transmissions and other equipment.

13.7.2 Demulsibility

Although the water washing of system oils to remove acids is no longer necessary and rarely practiced, it is usual to check that the oil will continue to release water in a series of repeated ASTM D1401 tests. The test is also used to check that the system oil will still release water when contaminated with cylinder oil containing high levels of detergent. Water shedding is finally checked using a small lubricating oil centrifuge to determine the number of passes required to reduce the water content from, say, 5 to 0.1%. Hydrolytic stability tests are used to check emulsion stability and additive stability in the presence of water.

13.7.3 Rust and Corrosion Protection

Protection against ferrous corrosion by sea water can be assessed by IP 135B in which a mild steel pin is suspended in a mixture of oil and standardised synthetic sea water for 24 h at 60°C. Other tests used include a static water drop test and a hydrobromic acid test.

Bearing metal corrosion is evaluated by the Mirrlees corrosion test in which test coupons are suspended in the candidate oil for 100 h at 140°C. The procedure evaluates the tendency of a lubricant to cause grain boundary attack and incipient corrosion on small specimens of:

White metal
Phosphor–bronze
Copper–lead,
Aluminium–tin

13.7.4 Oxidation and Thermal Stability

There are a considerable number of oxidation and thermal stability tests, mirroring the complexity of the processes themselves. Oxidation tests used include the Indiana-stirred oxidation test [22], the rotary bomb oxidation by IP 229 and other standard procedures such as IP 48, IP 280 and IP 306.

Despite their use only in diesel engines, marine oils are sometimes checked for oxidation tendencies in the Labeco L-38 gasoline engine, which measures viscosity thickening resulting from oxidation/polymerisation and the loss in weight of copper–lead bearings through acidic corrosion.

High-temperature coking resistance is checked by the panel coker test where an aluminium plate, held at temperatures ranging from 275 to 350°C, is splashed with lubricant and the deposited coke is weighed and rated. This procedure has many variations including methods to measure the effect of the oxidising effect of fuel oil contamination on lubricant stability.

13.7.5 Load Carrying

System oils to be used in crosshead engines equipped with power take-off, in addition to the general lubricating oil requirements, must have adequate load-carrying properties as specified by the engine builder. The requirements defined by the FZG gear test [23] can be met by the inclusion of low levels of ZDDP because of the low BN of alkaline system oils. The low BN is achieved by relatively small amounts of overbased alkaline detergents minimising the competition for metallic surface sites and so allowing the anti-wear agents to function effectively. Other tests used for screening purposes include the four-ball, Timken, pin-on-disc and Cameron Plint rigs.

13.8 Cylinder Oils

13.8.1 Introduction

Marine diesel cylinder lubricants are total loss lubricants. In their brief operational life their main functions are to provide a strong oil film between the cylinder liner and the piston rings, hold partially burnt fuel residues in suspension so promoting engine cleanliness, and neutralise acids formed by the combustion of sulphur compounds in the fuel. Marine diesel cylinder lubricants are therefore formulated to combat mechanical, abrasive and corrosive wear.

13.8.2 Colloidal Stability

The high base number of marine diesel cylinder lubricants requires the use of large amounts of overbased detergents. For example, a 70 BN cylinder oil contains approximately 25% wt overbased additives. In order to achieve specific formulation benefits, overbased additives such as calcium sulphonates and phenates are often mixed together. Unfortunately, the mixing of these additives in such high concentrations can cause interactions leading to colloidal instability and deposits, mainly of calcium carbonate. This must be avoided because if deposits occurred in practice they could cause blockages of feed lines, filters and lubricating quills. Marine quality additives with good colloid stability are selected through extended tests and accelerated centrifuge tests.

13.8.3 Acid Neutralisation

Despite the high base number of marine diesel cylinder lubricants, if all the sulphur compounds in the heavy fuel oil were converted to sulphur acids, only a small proportion of the resulting acid could be neutralised because of the relatively low volume of lubricant employed. Typical feed rates for fuel and lubricant are 120 and 1 g/bhp/h, respectively. At these feed rates and with a fuel containing 3% sulphur, a 70 BN lubricant could neutralise less than 1% of the sulphur acids formed if all the sulphur were converted into acids at the quoted feed rates. Fortunately, most of the sulphur is discharged with the exhaust gases as sulphur oxides.

Any acids that do form in the cylinder must be neutralised rapidly. Different overbased additives have different acid neutralisation rates and reaction rates can be increased by small additions of suitable additives. Several laboratory tests have been developed to compare neutralisation rates. Most are dependent on measuring the carbon dioxide evolved when sulphuric acid is added to candidate oils in laboratory glassware, both in the presence and absence of iron.

13.8.4 Spreadability

A single cylinder of a super-long stroke crosshead engine can have an area of up to 7 m^2. Cylinder lubrication is achieved by timed injection through approximately eight lubricating points spaced equidistantly around and near the top of the liner. The injection points are connected by moustached grooves to assist the oil to spread. Approximately 1 g of oil is injected every revolution or second.

Spreadability is determined in the laboratory by dropping small, known, weights of oil onto a flat metal plate held at an elevated temperature and measuring the area covered by the oil. The plates are normally machined from cylinder liners and the temperature is chosen to correspond to temperatures found at the top of the liner in service, e.g. 200°C. Base oils have good spreadability but this is reduced dramatically by the additives present in marine diesel cylinder lubricants. Spreadability can be increased by a limited number of additives.

13.8.5 Engine Tests

There are no standard test engines for assessing marine diesel cylinder lubricant performance. Lubricating oil companies have their own engines and procedures although the engine most commonly used is probably the Bolnes 3DNL, Table 13.8. The fuel is carefully selected to have high sulphur, Conradson carbon residue and asphaltene content but no catalytic fines. There is no set procedure for the Bolnes engine and at the end of the test the engine is assessed by in-house procedures for liner wear, ring wear and cleanliness. A matrix of tests is run to accommodate cylinder-to-cylinder and test-to-test variations.

Thin-layer activation has been used with the large cylinder oil test engines to give rapid screening of candidate oils. Oils can be assessed over periods of 10–12 h and a series of lubricants tested without dismantling or even stopping the engine. Cobalt-56, ^{56}Co, is a preferred gamma ray source and either ring or liner wear can be measured.

Table 13.8 Characteristics of Bolnes 3DNL engine

Type	Two-stroke
Cylinders, aspiration	3, Turbocharged
Speed (rpm)	500
P_{max} (bar)	120
B_{mep} (bar)	11.2
Bore (mm)	190
Stroke (mm)	350
Test duration (h)	75–200
Fuel	Heavy fuel oil

13.8.6 Field Tests

The final proof of a cylinder oil's performance is established by field testing using land-based and ship engines. Engines are assessed for liner wear, ring wear and cleanliness using a variety of instruments and procedures. Comprehensive engine inspections require the engine to be opened and the pistons lifted. This is not always convenient, particularly for the ship operator, and some lubricating oil companies use the Sulzer integrated piston ring wear detecting arrangement, SIPWA, to measure ring wear [24].

SIPWA was originally designed to enable the ship operator to (i) correlate ring wear with fuel treatment and take remedial action if necessary and (ii) safely pursue an economic fuel purchasing policy. The technique is ideally suited to be a research tool because it monitors wear without interfering with the operation of the engine. The patented piston ring is built up from two parts, the normal cast iron ring itself and a circumferential, non-magnetic bronze, wedge-shaped, element working surface, Fig. 13.3. This insert is arranged in a spiral from one butt end to the other and as the ring passes wears, the width decreases. A wear-dependent signal is produced every revolution as the ring passes the detector sited in the bottom of the liner. From measurements P_2–P_3 and P_1–P_2, the ring wear and ring position can be determined. By lubricating a multicylinder engine with two or more cylinder oils simultaneously, the performance of the oils can be compared directly under the same operating conditions.

13.9 Trunk Piston Engine Oils

13.9.1 Introduction

A manufacturer's range of trunk piston engine oils will include products with base numbers from approximately 15 to 50. The appropriate oil is then selected to match the sulphur content of the fuel being used. In service, the initial BN will fall fairly rapidly but will then stabilise. The stabilised BN is normally rather more than half the original value of new oil, ensuring good corrosion protection.

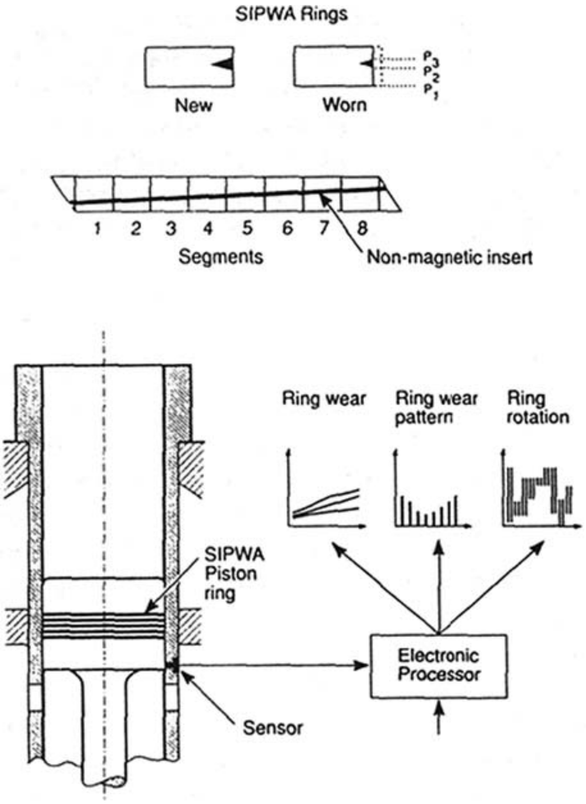

Fig. 13.3 Sulzer integrated piston ring wear detecting arrangement, redrawn and adapted from Sulzer Diesel Ltd. [24]

13.9.2 Filterability

Considerable care is required to achieve the appropriate formulation of detergency and dispersancy. Insoluble material, derived principally from combustion products, must be kept in fine suspension to avoid damage to bearings, etc. but at the same time the oil must release insolubles to the filter and centrifuges [25]. Oils are screened using laboratory filters of known pore diameter and distribution. Before final field trials the lubricants are checked in small marine lubricant centrifuges. Water has a strong influence on dispersancy and can cause insolubles to be deposited prematurely. The effect of water contamination has therefore to be checked.

13.9.3 Heavy Fuel Engine Tests

Trunk piston engine oils, even those with relatively low base numbers, easily surpass the normal diesel engine test performance requirement based on engines such as Caterpillar's single cylinder 1Y73 when it is run on distillate fuel. More severe tests have therefore been developed using the same or similar engines operating on heavy fuel oil. There are no standard industry tests and companies have perfected their own test procedures. The heavy fuel engine tests are designed to evaluate the performance of lubricants with respect to piston cleanliness, ring and liner wear, depletion and insolubles.

13.10 Analysis of In-Service Oils

13.10.1 Introduction

Frequent testing of lubricants in service helps to safeguard the machinery. Samples of lubricant submitted for analysis must be representative of the total oil charge and to assist ship's engineers the CEC (Co-ordinating European Council) has drawn up a Code of Practice [26]. The Code of Practice aims to ensure that oil samples are drawn correctly, fully identified, do not become contaminated and are properly packaged for dispatch to the laboratory.

For maximum benefit, testing must be conducted rapidly and for this reason many oil companies have developed proprietary and automated test methods for routine oil analysis. The methods are cross-referenced to standard methods and utilise modern analytical instruments. For example, the standard method for determining the water content of a lubricating oil sample is distillation but various proprietary methods have been developed based on the use of gas chromatography, near-infrared spectrometry and vapour pressure.

The use of non-standard methods can cause problems for ship owners and engine manufacturers in interpreting results. They also make it difficult to compare results from different laboratories. To reduce these problems, CEC have produced a document, CEC M-13-T-92, identifying well-established test methods that should be used if a dispute arises about the condition of a lubricating oil [27].

The tests carried out are designed to give the maximum information from the minimum number of tests with supplementary tests being carried out if the need arises. Interpretation of results and, where necessary, a recommended course of action are part of the lubricant supplier's responsibilities [28]. The reasons for carrying out tests and the information they can give are outlined in the following sections.

13.10.2 Density

Used for selecting the correct gravity disc for the lubricating oil centrifuge.

13.10.3 Viscosity

Changes in viscosity in service arise from either fuel dilution or suspended matter. Assuming no other adverse symptoms, changes in viscosity of ±20–25% can be tolerated. Contamination by marine diesel or distillate fuel reduces viscosity; contamination by heavy fuel oil increases viscosity.

In both cases the flash point of the lubricant is likely to be reduced. If increased viscosity is due to carbonaceous insolubles, both viscosity and insolubles can often be reduced by correct centrifuging.

13.10.4 Flash Point

Both marine diesel and heavy fuel oil have low flash points compared with lubricating oil, e.g. 60–100°C compared with over 200°C. The relatively low flash point heavy fuel oil is caused by the ‘cutter stock’, e.g. kerosene or gas oil, used to give an acceptable viscosity from the extremely viscous vacuum residues, visbroken residues, etc. Contamination by diesel or heavy fuel oil therefore normally reduces the flash point of the lubricant, although with heavy fuel oil the small amount of volatile matter can be driven off from the lubricating system.

13.10.5 Insolubles

The majority of insolubles are derived from the combustion products of the fuel and lubricant. Insolubles can also contain spent additives from the lubricant, e.g. calcium sulphate, and general debris such as rust, wear metals and contaminants from water ingress and air intakes.

Heavy duty detergent oils usually include ashless dispersants within their formulation to keep combustion contaminants in fine suspension to prevent damage to machinery. Warning limits for the insolubles content of trunk piston engine oils vary with the oil but in some cases levels of 5% can be tolerated. When high levels of insolubles are encountered, the fuel and fuel combustion systems should be examined.

13.10.6 Base Number

In service use, the base number, or reserve alkalinity, steadily declines until a plateau is reached. At this point the higher base number of the new oil, used for topping up, balances the acidic products of combustion. The plateau is usually rather more than 50% of the original base number and must meet the minimum level set by the engine manufacturer. If base number declines by more than, say, 60%, countermeasures must be taken dependent on the circumstances. In one-off situations, part of the charge can be replaced with a higher base number lubricant, otherwise the continuous use of a higher base number oil is recommended.

13.10.7 Water Content

The water content of system and heavy duty crankcase oils can generally be maintained below 0.2 and 0.5%, respectively. If water is detected, the first priority is to establish and correct the source of contamination. This is particularly true for sea water contamination because severe corrosion can occur very rapidly.

13.10.8 Wear Metals

Inductively coupled plasma, ICP, atomic emission spectroscopy has made the determination of wear metals very easy and used oils can be scanned for the presence of at least 20 elements in less than 1 min. Wear trends can be obtained by comparing wear metals from a series of samples. However, it should be noted that the accuracy of the determination can be limited by the particle sizes present.

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Chapter 14
Lubricating Grease

G. Gow

Abstract Grease lubrication is a complex mixture of science and engineering, requires an interdisciplinary approach, and is applied to the majority of bearings worldwide. Grease can be more than a lubricant; it is often expected to perform as a seal, corrosion inhibitor, shock absorber and a noise suppressant. It is a viscoelastic plastic solid, therefore, a liquid or solid, dependent upon the applied physical conditions of stress and/or temperature, with a yield value, σ_0. It has a coarse structure of filaments within a matrix. The suitability of flow properties of a grease for an application is best determined using a controlled stress rheometer for the frequency response of parameters such as yield, σ_0, complex shear modulus, G^*, phase angle, δ, and the complex viscosity, η^*.

Grease is formulated from a base oil, typically 85%, a thickener system at ~10% plus other possible ingredients imparting special properties. Base oils are usually paraffinic mineral oils with some synthetic base oils used. Thickeners are based either on metal soaps, particularly calcium and lithium, with complex soaps giving particularly good performance at higher temperatures. Inorganic thickeners include clay, silica gel and molybdenum disulphide. Polymeric thickeners include the polyolefins, PTFE and polyureas. Future demand divides into commodity, low cost, basic grease at one end of the market and increasing demands for higher performance, longer lasting speciality products at the other. Health and environmental considerations will increasingly determine the materials that can be used to formulate grease, more so as the EU Reach Directive and its associated regulations become effective, as will be the case in analogous ways for other trading areas.

14.1 Introduction to Lubricating Grease

The Nature and Use of Grease: Lubricating grease has been regarded by many prominent members of the oil industry as more of ‘an art’ than a science. One of the primary objectives of a new generation of lubrication engineers is to radically change this concept and start speaking the same language as other scientists. Grease lubrication is a complex mixture of chemistry, physics, tribology, rheology and

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today, health and the environmental sciences. Any ambitious research and development project will therefore eventually fail without extensive interdisciplinary co-operation and understanding.

Lubricating grease is a vital part of a great number of machine components. However, this is often forgotten or ignored by product designers. Lubrication specialists are called in to design projects at the very last minute, leading to serious problems which could perhaps have been avoided if the lubricant had been considered as an integral part of the total system right from the very start.

Economically speaking, lubricating grease is regarded as a commodity and, as such, it is often a low-price product. This means that the potential manufacturing profit is limited by the cost of resources, both capital and manpower, required to develop and produce the grease. Basic research into the fundamentals of grease lubrication is somewhat scarce in the academic community, presumably due to lack of funding. Most research takes place under the auspices of the international oil companies and their laboratory personnel are, by tradition, predominantly chemists. Whilst grease manufacturing is indisputably based on chemistry, the study of grease in practical situations, in which grease acts as a mechanical barrier between two moving surfaces, serving to keep them apart, leads invariably into the realm of physics and engineering. Looking for chemical answers to physical problems can only lead to questionable conclusions and compromises.

Lubricating grease is not a new product. Evidence from archaeological findings in the Middle East suggests that ‘the art’ of making grease was known at least 4000 years ago. The current generation of greases has some 60 years of history behind it. Clarence E. Earle’s patents on the use of lithium soaps in lubricating grease were issued in the early 1940s and well over 60% of lubricating greases produced in the western world are based on this technology. However, there is still a long way to go in lubricating grease technology [1]. A comprehensive study of all aspects of grease technology with the corresponding literature references is beyond the scope of this short contribution. There are numerous textbooks available on this subject [2–9]. Since the basics of lubrication will be dealt with elsewhere in this book, this chapter will focus on illustrating the difference between a grease and an oil and the advantages offered by a grease as opposed to a fluid lubricant.

According to the classical ASTM definition, lubricating grease is ‘a solid to semi-fluid product of a thickening agent in a liquid lubricant, other ingredients imparting special properties may be included’. This definition may be somewhat diffuse but it does establish one very important fact regarding composition and properties; grease is not a thick, i.e. viscous, oil, it is instead a thickened oil, a multi-phase system consisting of at least two well-defined components, a thickener (gelling agent) and a fluid lubricant. A more rheologically based definition is:

> *a lubricant which under certain loads and within its range of temperature application, exhibits the properties of a solid body, undergoes plastic strain*

> *and starts to flow like a liquid should the load reach the critical point, and regains solid body like properties after the removal of stress [10].*

This definition captures yet another very important point; grease is both solid *and* liquid depending on the physical conditions of stress, temperature, etc., and features an additional property compared to a pure liquid lubricant, a yield value, σ_0, the threshold level of shear stress or strain. Whereas the ASTM definition focuses on the structure and content and Sinitsyn's definition on the rheological properties, a more practical definition has been proposed which highlights the very purpose of using a lubricant and suggests that a grease can be classed as a 'deforce' [11]. This play on words comes from an abbreviation D4S or rather DESSSS, a 'dynamic energy saving, shearable, surface separator'. If an optimised lubricant can be seen as an attempt to keep surfaces apart using the minimum of energy, low friction, then this definition may well be the most relevant. However, modern greases are so varied in both characteristics and contents that the only accurate definition is, with apologies to Cheng [12]:

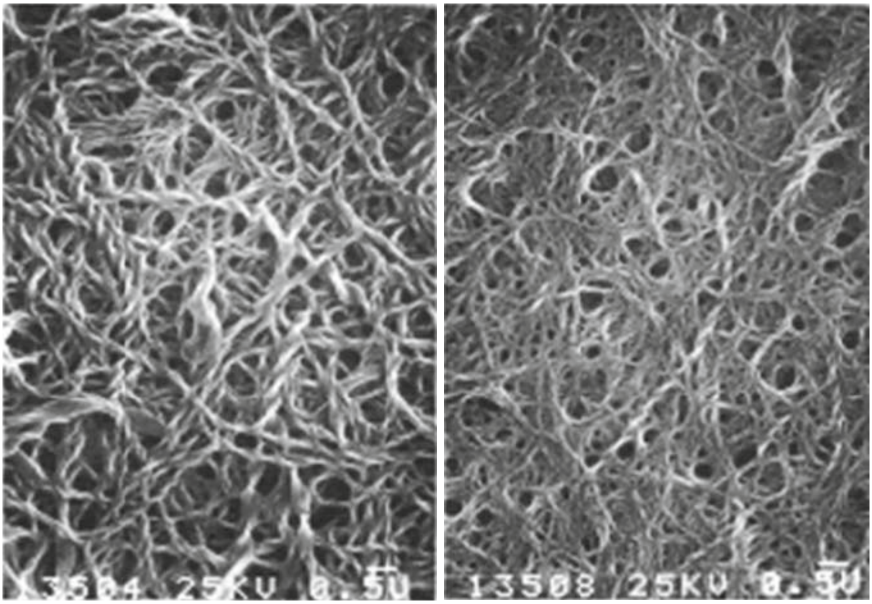
> *lubricating grease is what grease makers make.*

14.2 Structure and Rheological Properties

14.2.1 Structure of Grease

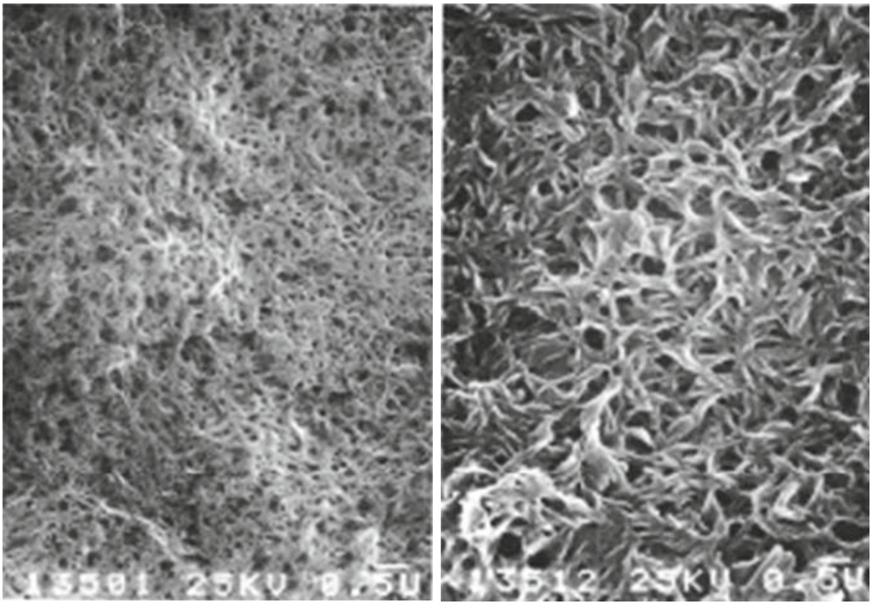
Lubricating grease is perhaps best described as a viscoelastic plastic solid and, as such, is extremely complicated in both physical and chemical characteristics. The separate components are not in chemical solution but co-exist like water in a sponge. This popular illustration, in which the thickener is the sponge and the fluid lubricant is the water, is, of course, not a strictly valid scientific description. But it is useful in conceptualising certain problems arising from the use of this type of material. How to pump, or filter, a sponge full of water can be an interesting scientific challenge. What happens to a sponge full of water if it is exposed to a squeezing action, as in roller bearings, or to centrifugal forces, as in high-speed couplings? SEM photographs of the fibre structure of soaps commonly used in grease manufacturing reveal that the concept of the sponge is not totally invalid, see Fig. 14.1, and the challenge becomes how to quantitatively characterise the different 'sponges'. Figure 14.1 shows the effect of formulation modifications for a lithium 12-hydroxy stearate in:

(a) mineral oil grease as its coarse structure,
(b) its finer structure of the same formulation,
(c) the structure for the same lithium compound in a synthetic ester and
(d) the effect of modifying the lithium compound in a mineral oil.



Lithium-12-hydroxy stearate in a mineral oil , ‘normal coarse structure’

Lithium-12-hydroxy stearate in a mineral oil , ‘finer coarse structure’



Lithium-12-hydroxy stearate in a synthetic ester, ‘very fine structure’

Modified lithium-12-hydroxy stearate in a mineral oil, as a ‘lithium complex grease’.

Fig. 14.1 SEM photomicrograph of lithium 12-hydroxy grease structures

14.2.2 The Rheology of Grease

Grease is not a thick oil but a thickened oil. The grease matrix is held together by internal binding forces giving the grease a solid character by resisting positional change. This rigidity is commonly referred to as 'consistency'. When the external stresses exceed the threshold level of shear (stress or strain) – the yield value, σ, – the solid goes through a transitional state of plastic strain before turning into a flowing liquid. Consistency can be seen as the most important property of a lubricating grease, the vital difference between grease and oil. Under the force of gravity, a grease is normally subjected to shear stresses below the yield value and will therefore remain in place as a solid body. At higher levels of shear, however, the grease will flow. Therefore, it is of the utmost importance to be able to determine the exact level of yield. This is obviously a time-dependent factor and the time scale must be chosen carefully, dependent on the information required. At present, consistency is still measured by means of a cone penetrometer, by ASTM D 217, and greases are classified according to the so-called NLGI system [8]. This classification is universal and the great majority of greases are used and chosen solely on the basis of their NLGI grade. This method is, however, scientifically unacceptable, since the materials are exposed to varying levels of shear rates and the resulting figures should therefore never be compared to one another [13]. Penetration measurements can be interesting for simplistic production control to ensure that a given product has the same consistency as a previous batch but to use the figures to predict performance under dynamic conditions involves dangerous assumptions.

The distinction between a liquid and a solid can sometimes be very diffuse. Materials which exhibit both elastic and viscous tendencies under varying conditions are termed *viscoelastic*. There is equipment available which is suitable for testing viscoelastic properties but it is often expensive and requires qualified personnel. Depending on the different applications, the grease trade has used certain standard methods for the determination of rheological properties, examples are:

- 'Apparent Viscosity', ASTM D 1092,
- 'Measurement of Flow Properties at High Temperatures', ASTM D 3232,
- 'Determination of Flow Pressure', DIN 51805 and
- 'Cone Penetration', ASTM D 217.

Other non-standardised tests such as sliding plate and ventmeter systems have also been adopted. The approach to rheology has at last become more modern and the use of modern viscometers [13–19] is a positive development. An attempt to find one single method of measuring the rheological properties of grease is, of course, as doomed to failure as trying to find one method of determining all the chemical properties. Suitable rheological test methods have been addressed in the ELGI (European Lubricating Grease Institute) Rheology Handbook [20]. Units of viscosity pertaining to non-Newtonian materials are meaningless without the corresponding values of shear rate and it is therefore of the utmost importance to define the shear rates in absolute terms. In different pump systems, as for instance in centralised lubrication, greases are subjected to shear rates perhaps as low as $10^{-1}\,s^{-1}$. On the other hand, in the EHD regimes of heavily loaded bearings and gears, the shear rates may be as high as 10^6–10^8 s^{-1}. Intermediate values are probably less significant in practical terms. The rheological test systems of the past, still used in many grease laboratories, are unfortunately in the wrong shear rate range to be able to predict functional performance.

For the exact measurement of yield, a modern controlled stress rheometer is a very useful instrument [21, 22]. For lower shear rates, below $1\,s^{-1}$, a rheometer capable of both rotary and oscillatory viscometry is necessary. The oscillation mode also permits the measurement of elasticity and the phase angle, δ, together with the complex shear modulus, G^*, providing vital information as to the dynamic properties of any given product. An example of the information that can be obtained using a controlled stress rheometer is given in Fig. 14.2 for the frequency response of a lithium grease at 25°C in terms of the complex shear modulus, G^*, the phase angle, δ, and the complex viscosity, η^* – note the logarithmic plot for the frequency axis.

Grease 'softens', i.e. becomes less viscous, with increase in temperature. This temperature dependence is analogous to the viscosity index, VI, of fluid oils. It is

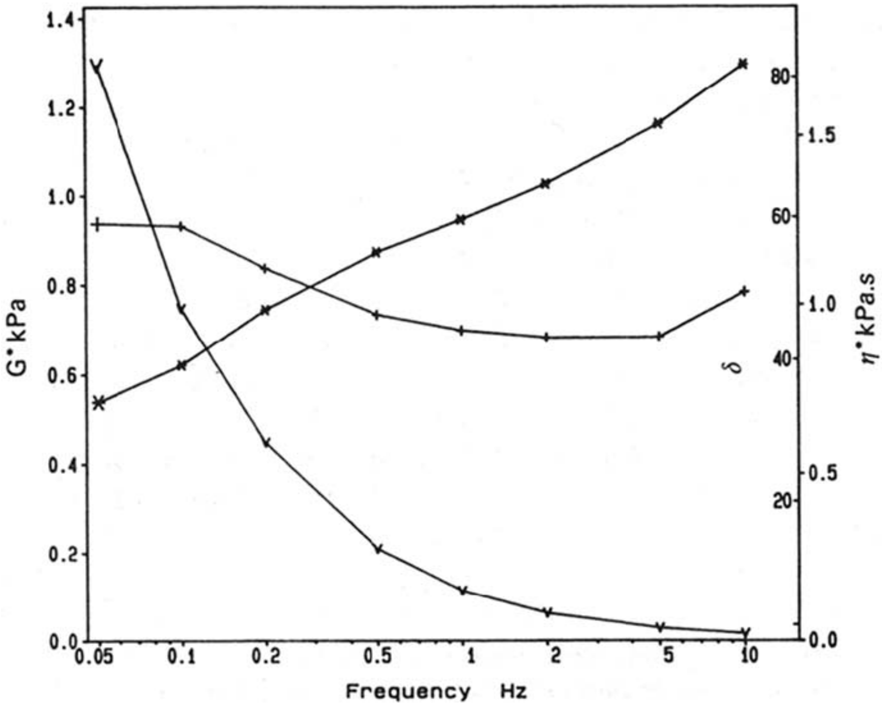


Fig. 14.2 Frequency dependence of the complex shear modulus, G^* (x), phase angle, δ (+), and complex viscosity, η^* (v), for a lithium grease at 25°C

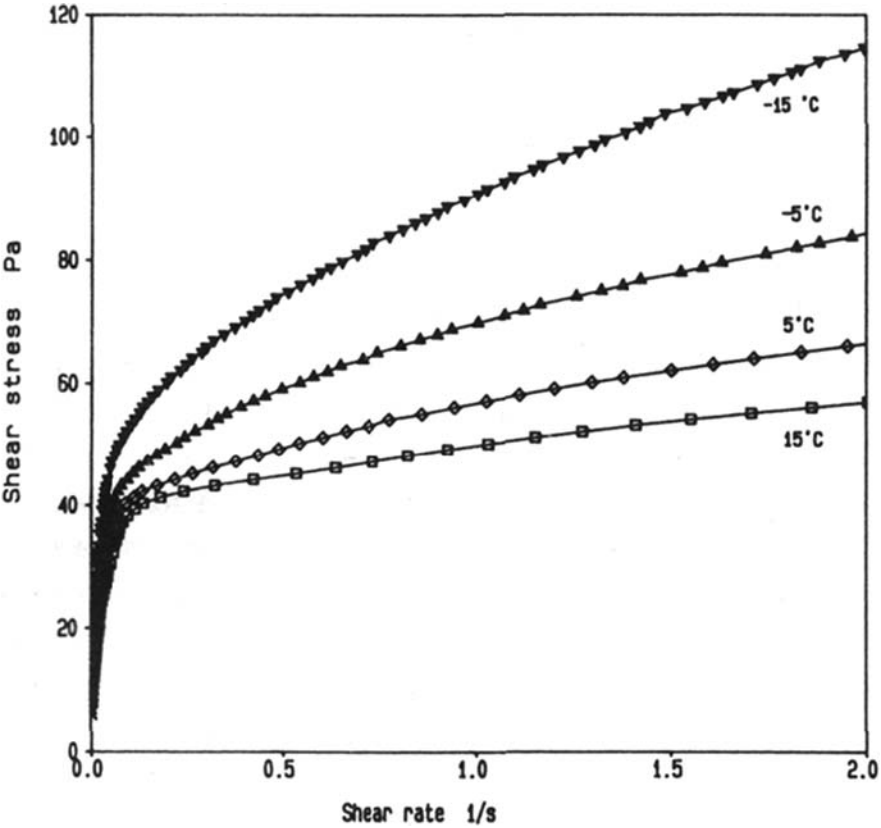


Fig. 14.3 Temperature and shear rate dependences of the yield value for an NLGI 00 lithium complex grease specially formulated for automotive centralised lubrication systems

readily measured over a range of temperatures using a controlled stress rheometer, Fig. 14.3, shown as a function of shear rate for the yield value of a lithium complex grease between –15°C and +15°C.

Previous investigations have often involved the extrapolation of higher shear rate measurements into the low shear rate range, and this can lead to very misleading conditions. Once again, the time factor becomes very important and time scales in excess of, say, 1 s can stretch the patience of a maintenance engineer with a grease gun, leading to the need for the concept of a ‘practical yield value’ instead of a purely academic one. For the very high shear rate range, a slit viscometer, for instance, would be an interesting possibility but few are commercially available. Other types of instruments have been tested by technical institutes and universities. One example is the impacting ball apparatus at Luleå University in Sweden [23, 24] and an improved ball and bar apparatus [25]. Results from the former method give a simple way to obtain comparative information on the maximum shear stress–pressure coefficients for base oils and thickeners used to make greases (Fig. 14.4).

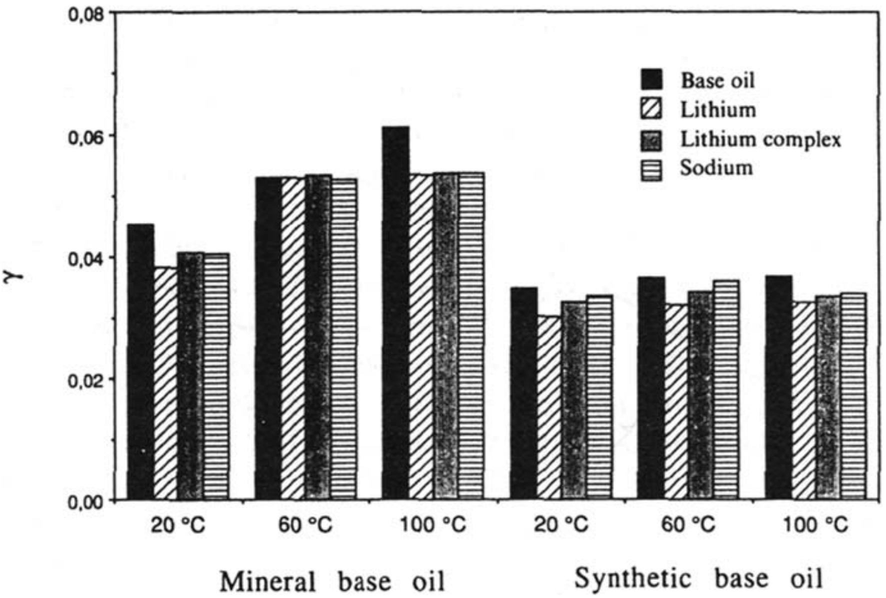


Fig. 14.4 Limiting shear stress–pressure coefficients, γ, of six different greases formulated from three thickeners and two base oils, at 20, 60 and 80°C, from [24]

14.3 The Chemistry of Grease

14.3.1 Introduction

The chemistry of lubricating grease is also very complicated but has already been investigated in a detailed way. A concise summary is provided in the NLGI Lubricating Grease Guide [8], together with a basic description of the most common raw materials used. Grease contains at least two components:

– the base fluid and
– the thickener system.

A typical multipurpose grease can contain about 85% base fluid, 10% thickener and 5% ‘other ingredients imparting special properties’, ASTM 1961.

14.3.2 Base Fluids in Grease

The base fluids used in grease can be divided into two main groups, mineral oils and synthetic fluids, although natural oils are experiencing somewhat of a renaissance because of environmental considerations, the European Union ECO-label, as an example.

A wide range of lubricant base fluids are used in grease technology. However, the largest segment consists of a variety of products derived from the refining of crude oil and downstream petroleum raw materials. These mineral oils can contain a very wide spectrum of chemical components, dependent upon the origin and composition of the crude oil as well as the refining processes to which they have been submitted. There are three basic groups of mineral oils: aromatic, naphthenic and paraffinic. Historically, the first two have represented the principal volumes used in grease formulation, largely due to availability but also due to their solubility characteristics.

However, concerns about the carcinogenic aspects of molecules containing aromatic and polyaromatic ring structures have led to their replacement by paraffinic oils as the mineral fluids of choice. The oil components of grease must offer a range of appropriate properties in order to fulfil their roles in a wide range of applications.

Viscosity and its temperature dependency are obviously key requirements, but loss of volatile components and oxidation stability can also be important selection criteria. In the latter case, the response of the base oil to antioxidants also needs to be taken into account.

Perhaps the most important factor in the choice of the oil phase is *solubility*. This criterion affects both the manufacturing process and the final matrix structure of the grease and is vital to the performance characteristics in any particular application. The decline in the use of oils containing aromatic and polyaromatic components has reduced the range of solubility characteristics available to the grease technologist. However, naphthenic oils contain not only polyaromatics but also similar, less toxic, polycyclic compounds without a benzene ring structure. Using modern selective refining techniques, it is possible to remove only the unwanted components and produce oils with low toxicity. Thus, these severely refined oils provide a range of beneficial solubility properties, similar to conventional types of naphthenic oils but without the toxicity problems. Modern base oils in lubricating greases are therefore often a blend of severely refined paraffinic and naphthenic oils, designed to provide the final product with the appropriate characteristics of mechanical stability, lubricity and dropping point.

Synthetic fluids can be tailored to provide properties that might be impossible to achieve using conventional mineral oil products. Typical examples are applications with a wider range of operating temperatures or where chemical resistance is required. Furthermore, compatibility with rubber or plastic components and seals, the lubrication of non-metallic surfaces and improved electrical properties are all areas where synthetic base fluids can make a contribution. Environmental considerations, such as biodegradability, are increasingly becoming factors influencing the selection of synthetics. There are several groups of synthetic base fluids that find applications in grease and most of these are specifically designed products, rather than the oil distillate cuts that comprise the mineral oil range. These include synthetic hydrocarbons such as polyalphaolefins and alkylated aromatics, esters, polyglycols, silicone oils, perfluoropolyethers and many other types of fluids. The possible advantages and disadvantages are not given here because they are not exclusive to grease and are covered elsewhere in this publication.

14.3.3 Grease Thickeners

Developments in thickeners have been fundamental to the advances in grease technology. The contribution of thickeners has been so central to developments that many greases are often classified by the type of thickener used to give the structured matrix and consistency. The two principal groups of thickeners are metal soaps and inorganic compounds, soap-based greases being by far the most widespread.

The earliest greases were made by reacting lime with vegetable oils, or animal fats, in the presence of water, to produce a *calcium soap* of the natural fatty acid. The resulting thickened oil was adequate for simple lubrication tasks such as cart wheels and water wheel shafts and bearings. These simple calcium greases were only found to be inadequate when the development of the steam engine led to higher operational temperatures. The melting point of a calcium grease is around 100°C and higher running temperatures proved to be too challenging at that time.

Nevertheless, calcium greases of this type are still in use today for less demanding applications and their manufacture is very similar to the processes used over 100 years ago. Calcium soap is produced with a small residual water content which acts as a stabiliser for the soap matrix and thus provides the required structure of the thickener. In some operating conditions, when the temperature is constantly above 50°C, water evaporation may result in the complete breakdown of consistency in the grease and it will revert to a fluid state.

Conventional calcium greases have good adhesive properties and they are extremely water resistant. At relatively low cost, their use today continues in cool, wet conditions such as in marine applications, propeller housings and water pumps.

Sodium soaps, which are very similar to domestic soap used for hygiene purposes, were found to have higher melting points than calcium soaps. Greases based on sodium soaps were fundamental in the lubrication of steam engines and the early machinery of the industrial revolution. Sodium grease has an operating capability up to temperatures of approximately 110°C and it became the foremost high-temperature grease at the beginning of the 20th century. Unfortunately sodium greases have three significant weaknesses. They are water soluble, like domestic soap, and also suffer from hardening in storage. Furthermore, due to the large fibre size of traditional sodium soaps, they do not contribute lubricity to the grease. This inadequacy results in poorer load-carrying capabilities and means that a base oil of higher viscosity is needed to provide heavy duty properties. The use of sodium grease is declining rapidly, but occasional applications are still found in enclosed gears and couplings.

Greases based on *aluminium thickeners* were developed at the same time as sodium greases as engineers searched for improved lubrication for steam engines. Aluminium thickeners and, in particular aluminium stearate, seemed to offer a grease with both water tolerance and a higher temperature capability. Unfortunately, aluminium-thickened greases have a major weakness in that they are extremely sensitive to shear. They are easily broken down mechanically, losing both their consistency and lubricating capability. Aluminium stearate grease can still find applications in low-shear simple plain bearings and as a chassis grease but has generally been replaced by more modern products.

In the first half of the 20th century, mechanical engineers had a relatively limited choice of grease types to cater for an increasingly challenging set of lubrication needs. Traditional calcium, sodium and aluminium greases were asked to cover all of the requirements. Catalysed principally by developments in the aircraft industry during the late 1930s, the introduction of *lithium-based greases* came as a very significant step forward, with patents issued to Clarence Earle in 1942–1943. For the first time, lubrication engineers had access to a grease which could be classified as truly multipurpose. Early lithium soaps were made from simple stearic acid, derived principally from beef tallow. Today, almost all lithium greases are based on the castor oil derivative, 12-hydroxy stearic acid, according to the Clarence Earle patents. The capabilities of lithium grease include excellent mechanical stability, good water resistance and reasonably good high-temperature performance, up to 120°C. This combination of benefits did not previously exist in the 1940s. During the second half of the 20th century, lithium greases replaced the earlier greases in the great majority of applications. The only real disadvantage with lithium-12-hydroxy stearate grease is pumpability at low temperatures; this can present a difficulty in centralised lubrication systems at temperatures below –10°C. Lithium soaps are very elastic and this property can affect mobility in long supply pipes.

A more recent development in calcium grease is the use of a soap that is not stabilised by water. This allows an upper operating temperature of 110°C, similar to sodium or even lithium greases. In addition to the temperature benefit, *anhydrous calcium* greases offer the advantages of traditional calcium greases, excellent adhesion, low-temperature lubricity and water resistance. Anhydrous calcium thickeners are normally based on 12-hydroxy stearic acid, just like their lithium counterparts and the resulting grease offers excellent mechanical stability. These greases are used widely in Europe for applications such as marine, agriculture, forestry and construction equipment.

The availability of a range of soaps, based on different metals, encouraged grease formulators to investigate the effect of mixtures in the final grease. Little benefit was found from this *mixed-based* approach, although compromise mixtures such as lithium–calcium have found some special applications.

A much more rewarding approach over the past 30 years has led to a range of so-called ‘*complex soaps*’. Derivatives of a single metal reacted with a combination of different types of acids can be crystallised into the same fibrous thickener structure. The principle advantage of complex greases is their ability to withstand high operating temperatures.

Aluminium complex greases have dropping points above 240°C, are highly water resistant and offer good lubricating properties at high temperatures. Furthermore, a low thickener concentration can provide the required grease consistency and this leads to excellent pumpability. This combination of properties has made aluminium complex grease popular as a steel mill lubricant. Their disadvantages centre on a tendency to harden under shear and their poorer mechanical stability in comparison to lithium greases. In this respect, they are similar to conventional aluminium stearate greases.

Calcium complex soaps were developed at the same time as aluminium complex greases and found favour due to their load carrying and extreme pressure capabilities. Their high-temperature performance was also found to be similar to aluminium complex greases with dropping points above 250°C. Their extreme pressure capability is provided by integral components of the co-crystallised soap structure: calcium acetate, calcium sulphonate or similar calcium derivatives are crystallised into the thickener structure. In contrast to aluminium complexes, a very high soap content is required to provide a given grease consistency and this can detract from pumpability. Calcium complex greases also have a tendency to harden in storage. More recent *calcium sulphonate complexes* also offer excellent water resistance, coupled with good high-temperature performance and load-carrying capacity. Their lubricating performance at more usual operating temperatures can be somewhat poorer, however.

Lithium complex greases have been finding increasing popularity over the past decade. The most commonly used complexing agents are dimer acids such as azelaic, adipic or sebacic acids but other substances, such as boric acid, have also been used. With dropping points above 300°C, this type of grease can withstand peak operating temperatures of up to 240°C for short periods of time. Continuous temperatures of 150°C should not present a problem for grease formulated with mineral oils; service temperatures of up to and in some cases exceeding 200°C are possible using synthetic base stocks. This excellent high-temperature performance results from a high melting point, coupled with the very dense fibre structure of the soap matrix. Very small polar fibres strongly bind the base lubricant providing excellent protection against oxidation due to low heat transfer throughout the matrix. According to the 2005 NLGI Grease Production Survey Report [26], 2004 statistics say that worldwide 15%, in Europe 10% and in North America >33% of the grease market is now held by lithium complex products. Typical applications are in the steel and paper industries, where elevated temperatures are commonplace. In cars and trucks, the grease is used in hub units, where the temperatures generated in modern brake systems have increased significantly. The excellent pumpability of lithium complex grease has led to its use in centralised lubrication systems on trucks and heavy equipment, particularly for cold climate applications.

Increasingly, lithium complex grease is regarded as the new generation, multipurpose grease with a wide temperature range, replacing traditional lithium products. This trend is enhanced by the broad compatibility of lithium complex with other grease types.

Inorganic Solid Thickeners: Substances which are essentially insoluble in the base oil can also be used as thickeners in grease formulations. Bentonite and hectorite clays, silica gel, graphite, polyethylene and polytetrafluoroethylene (PTFE) have all found applications. Fine clays, particularly bentonite clays, were used in grease formulations from the beginning of the 20th century, primarily in an attempt to improve high-temperature performance. The use of clay as the gelling agent results in a grease that does not melt or drop at high temperatures. However, the lack of a fibrous matrix structure does limit the stability of clay-based greases. Furthermore, the deleterious effects of oxidation can still occur in the base oil at elevated temperatures. Oil oxidation and separation can result in a residue of abrasive clay being deposited on the machine surfaces. However, clays still find applications for the gelling of highly viscous base fluids, such as bitumen, to produce compounds for use in open gear systems.

Silica gel, the methyl derivative of silicon dioxide, offers similar properties to clay in grease formulations. These greases were originally developed for the lubrication of small mechanical devices operating at low temperatures, for example, in aircraft. When centralised lubrication systems in heavy vehicles were introduced, silica gel and clay-based greases gained popularity due to their lack of elasticity and the resulting ease of pumpability. However, oil bleed, separation and the inherent instability of inorganic-thickened formulations caused blockages in feeder lines and dosing modules. The use of these thickeners was abandoned in favour of other greases such as lithium complex. Silica gel greases still find applications in the lubrication of aluminium and some plastics. In these cases, the use of metal soap thickeners is avoided due to the possibility of a reaction between the soap metal ion and the machine component.

Graphite – Greases based on graphite as the thickener are used almost exclusively for extremely high temperature applications. The graphite is dispersed in a carrier fluid that decomposes or evaporates in use, leaving the graphite as a lubricant. The fluids frequently used are polyglycols. Storage stability is limited as this type of formulation hardens with time. Typical applications are bearings in ovens and process equipment in steel mills.

PTFE – Inert base fluids, such as perfluoropolyethers, are used as lubricants in aggressive environments and require a PTFE thickener that is equally inert. Applications for this type of grease include contact with aggressive solvents and strong acids and alkalis. Inert grease of this type is also used to lubricate pumps and valves for oxygen and nitrous oxide in hospitals, where contact with other greases could pose a fire or explosion risk. Components containing sensitive or reactive plastics, rubbers, or ceramics can also be lubricated with this type of fluorinated grease. PTFE greases operate well under low pressure, such as in vacuum pumps and high-speed bearings in vacuum environments (space).

Polymer thickeners are becoming increasingly more interesting. The most commonly used substances in this context are different types of polyureas. This special polymer thickener system is normally a reaction product between different types of iso-cyanates and amines. *Polyurea greases* exhibit extremely good high-temperature performance and have, in many cases, become the preferred choice for filled-for-life applications in both bearings and joints. On the other hand, drawbacks such as poorer performance at ambient temperatures and the toxic nature of raw materials have limited their development into a more multipurpose product. In 2004, they represented less than 5% of the global market but, locally, in Japan, an impressive 21%. New developments in preformed polyurea powders can facilitate production for greasemakers in that the risks in the handling of toxic raw materials can be totally eliminated.

Although not very common, *polyethylene* and other similar polymers and waxes are used in very specific applications. In circumstances where very high centrifugal force or very rapid acceleration apply, a traditional ‘sponge’ matrix grease fails. Separation of the thickener and base fluid components occurs rapidly, immediately reducing lubricating ability. Polyethylene can be produced with a density very close to that of the chosen mineral base oil and separation does not occur. High-speed flexible couplings are lubricated with this type of grease. Yet another new and innovative type of grease being introduced into the market is based on a polymer (*polypropylene*) thickener with an optimised crystalline–amorphous balance. This type of grease offers many advantages over standard multipurpose greases: controlled oil bleed, extended service life, resistance to water and aggressive chemicals, enhanced additive response and not least a high film thickness in the track (efficient surface separator).

The properties of a lubricating grease can be modified by the incorporation of *additives* into the basic structure. In the ideal, hydrodynamic, situation, where the base grease keeps the metal surfaces apart, the need for additives may be minimal, but a grease is often much more than a lubricant. It is also expected to perform as a seal, a corrosion inhibitor, a shock absorber, or even a noise suppressant and most modern greases contain an additive package of some kind or another. There are many synergistic effects between the different types of materials available but solubility is once again a decisive factor. To be able to perform in fluid oils, the majority of additive systems have an optimised solubility in mineral oils. This is a necessity for oils in order to prevent sedimentation and/or phase separation. The same does not hold true for greases. In fact optimised solubility may be a disadvantage. To begin with, grease ‘at rest’ is a solid body so even completely insoluble substances such as MoS_2, graphite and titanium dioxide can be dispersed into the matrix. There is one major problem however and that is very few liquid additives perform well in greases and one explanation offered is that many of them are ‘locked’ into the oil phase. Most soap structures are highly polar in character and will compete with the additives for access to the metal surfaces. In most cases, the soap wins and covers the surfaces with a thin layer of fatty material. The additives dissolved in the oil cannot reach the metal surface and therefore have no effect. Insoluble additives may well be better since they will be dispersed in both phases and will at least have a theoretical chance of reaching the metal surface. The best place for the additives to be is on the soap structure itself which is why certain complex greases perform so well in, for instance, EP-tests.

14.3.4 Grease Manufacturing

The manufacturing of modern lubricating greases on a large scale involves, more often than not, a complicated saponification process requiring a high level of investment in both capital resources and manpower [27]. The number of commercial grease plants is steadily decreasing because of two major factors:

- a major rationalisation within the lubricants market and
- the cold economical facts of investing in the production of a product perceived to be a low-price commodity.

There are very few hypermodern grease plants, most of the current facilities originating from the 1950s or even earlier. The saponification process is carried out in two different types of production units, in batch production in open or pressurised kettles or 'Contactors' and in continuous production through small reaction chambers. Because of the nature of the business, this second type of continuous production is slowly disappearing since it is geared towards the manufacture of large volumes of one and the same product. The chemistry is the same in both cases. Most thickener systems are produced in situ by saponifying fatty acids with metal hydroxides in a portion of the base oil and in the presence of some water. The temperature is raised to the reaction temperature, kept there for a suitable period of time and then, in most cases, heated up to an even higher temperature to dehydrate and melt the soap at >200°C. The bottleneck of any grease manufacturing is the cooling process since lubricating greases have poor heat transfer properties. On cooling, the soap crystallises into its characteristic fibre structure (sponge) and the cooling rate is often vital in achieving the required properties. So speeding up the process is often not desirable. In order to optimise this stage, the cooling is often promoted under continual stirring. No matter how smoothly the cooling operation proceeds, the resulting mass is a relatively lumpy mixture and must be homogenised. This can be done in a multitude of ways, by pressure valves, tooth colloid mills and high-pressure homogenisers. The finishing process in which the additives are introduced, the consistency adjusted to the required level and the whole mixture homogenised is supplemented by a de-aeration unit, special filters and a whole array of packing systems. Different greases require different manufacturing methods and each grease plant has its own particular detailed technology.

Modern lubricating greases contain a wide variety of different chemical substances from complicated mixtures of natural hydrocarbons in the base oils, through well-defined soap structures, polymer solutions and even complex organic molecules in the additives, to simple chemicals such as carbon black and calcium carbonate. If formulations are regarded as proprietary and confidential, then the manufacturing processes must be classified as top secret. The 'art' of making grease has more to do with the making than the formulation.

14.4 Applications

14.4.1 Introduction

'Grease is quite simply better than oil' – this can be considered somewhat of a rash statement but there is more than an element of truth in the claim. Grease is highly elastic so its use as a brake fluid or in power transmission is more than questionable.

In addition, it cannot be used as a coolant since it has inferior heat transfer properties. As a pure lubricant, however, grease does have many advantages over fluid oil. The major advantages of grease over lubricating oil focus on four basic capabilities.

14.4.2 Grease as a Lubricant

Grease as a lubricant involves the properties of the base oil, the thickener and any functional additive. Because of its solid character, lubricating grease stays in place and can act as a reservoir of lubricant. This means that grease-lubricated components do not require relubrication intervals as short as fluid oils and that grease provides a certain degree of lubrication even if maintenance has been overlooked or forgotten over a considerable period of time. Therefore, replenishment mechanisms are critical for optimised performance and recent studies into these phenomena have given a new insight into grease functionality [28–30]. Figure 14.5 shows the filamental/fibrillar structure of grease in a film in the track of a roller moved across a greased flat surface. Grease has also superior high temperature and load-carrying properties because of the higher dynamic viscosity and elasticity provided by the thickener system. At low temperatures, the multi-phase system facilitates movement by preventing the characteristic crystallisation of paraffin waxes in the base oil and by allowing deformation to take place not only within the different phases but also

Fig. 14.5 The filament/fibrillar structure of a grease film in the track of a roller

in the boundary between the separate phases, as a lubricant, involving the properties of the base oil, the thickener and any functional additive.

14.4.3 Grease as a Sealant

Grease as a sealant is used to protect working surfaces from the effects of contamination by gases, liquids or solids, The consistency of grease prevents both fluid and solid contaminants from entering the system and also eliminates problems with dripping and leakage. In addition, grease facilitates the choice of mechanical seals. All this allows more freedom in design possibilities.

14.4.4 Grease as a Matrix

As a matrix, grease provides a carrier for a wide range of beneficial additives and to improve specific performance capabilities of the grease. Grease can perform as a carrier for certain insoluble substances such as MoS_2 and graphite. This is possible because the base material is solid and there is no problem with sedimentation, solvency or compatibility. These additives can be evenly dispersed throughout the multi-phase system.

14.4.5 Grease as a Corrosion Inhibitor

As a corrosion inhibitor, grease acts both directly as a sealant and indirectly as a matrix for corrosion-inhibiting additives. The consistency of grease and its ability to adhere to metal surfaces (tackiness and polarity) prevent reactive liquids from coming into contact with the metal surfaces and causing corrosion. Lubricating greases can also absorb considerable quantities of water, or cutting fluids, emulsions, industrial coolants etc., and still perform satisfactorily as a lubricant. Corrosion inhibition can be further enhanced by the inclusion of special additives.

14.4.6 Benefits of Grease

The benefits of grease to the user are significant, including reduced wear, extended relubrication and service intervals, less vibration and noise and lower energy consumption, all of which have the potential of contributing to a considerable reduction in total maintenance costs. In addition, if the grease technologist is able to exploit the wide flexibility of formulation possibilities, the range of operating conditions in which a grease can offer optimum performance can be greatly expanded.

All these factors contribute to grease being an excellent lubricant and it is often quite simple to choose the right product for any given application. On the other hand, in a modern highly technological society, there are many factors to be considered and the art of choosing the right grease may well become a complex problem.

A modern high-quality multipurpose grease can be said to cover up to 80% of all applications where grease lubrication is required. For the remaining 20%, special greases are necessary depending on three very important parameters:

– the component to be lubricated,
– the temperatures involved and
– the surrounding environment.

A conventional lithium-based multipurpose, NLGI 2 grade grease is often adequate for the lubrication of plain and rolling bearings working under normal conditions within a temperature range from –20°C to +120°C. Special greases are required for special applications such as different types of machine elements, e.g. gears, instruments, couplings, slides, and for high temperature, low temperature, low speed, wet applications, vibrations, in centralised lubrication systems, especially on automotive equipment. There are grease applications in special environments such as in the foodstuffs industry, or where there is contact with radiation, oxygen or other highly reactive chemicals, or if there are special cleanliness (filtration) requirements. Care for the natural environment also puts a special focus on biodegradability and other toxicological issues in loss-lubrication situations. The ways of solving specific lubrication problems vary in different parts of the world and from company to company, dependent on the technologies available.

14.5 Future Trends

Almost 70% of the lubricating greases manufactured and used within our industrialised world are based on lithium technology, invented and patented by Clarence Earle in the early 1940s. These products have, of course, been adapted and improved since then, but a great deal of the so-called ‘development’ has focussed on the addition of a wide variety of different chemical additives to compensate for the poor performance of the base product, i.e. different soaps as thickeners. There have been significant steps forward on a smaller scale or in limited regions and markets but the great majority of lubricating greases used today are based on a patent that was filed almost 60 years ago. On the other hand, this provides a certain degree of security in that most of the present-day conventional universal greases are based on a well-known, well-tried product with a long history of successful application.

For a number of reasons, the consumption of lubricating grease has stagnated in both Europe and North America due to better products, more effective systems, better maintenance routines, smaller machine elements, environmental concerns, etc. These trends, combined with the fact that grease is definitely not a significant volume product for the major oil companies at 3% of lubricants on average, have meant that the resources available for research and development and, in many cases even production, have been cut back continuously beginning sometime in the 1960s.

In the 1970s and 1980s the trend was towards producing THE GREASE, i.e. one product that could cover as wide as possible a range of applications, temperatures and surroundings. This resulted in the development of super multipurpose wide temperature range greases and there was no limit to the superlatives used in marketing and promotion. Technically speaking, this was an advantage in, for instance, industrial maintenance, since the number of greases used on any one particular site could be reduced and the risk of choosing the wrong product minimised. Economically speaking however, this proved to be a trap. For the simpler run-of-the-mill applications, this commodity multipurpose/extreme pressure grease was quite simply too expensive. And with the exponential development of state-of-the-art manufacturing techniques, the product just was not good enough to solve the real problems and challenges of modern lubrication. In his ‘Mapping the Future Marketplace’, Kotler [31] forecast in 1997 that:

> *high income customers will demand high quality products and personalised service. At the opposite end, will be people who just want basic, no-frills products and services at the lowest possible price.*

So there is no middle option. In the lubricating grease market, this trend is becoming more and more obvious. For the commodity MP/EP grease market, the economics are the dominant decision parameter and grease makers need to design products, processes and logistics to meet this ever-sharpening climate. Here, there is a basic technology with many well-known products and brands on which the industry relies and these will maintain and perhaps even strengthen their positions in an ever-globalising market. At the other end, the high-tech OEMs are putting ever-increasing demands on both functionality and the service life of lubricants. Relubrication can cost much more than the choice of more expensive but more efficient grease. These products should, in theory, last longer than the components in which they are expected to perform.

Another factor influencing the choice of more advanced lubricating greases and which has become a major driver in the development process is the *environment*, both in terms of the working environment, surroundings, health issues, etc., and the natural environment in respect of loss lubrication and ecotoxicology. These issues affect even the manufacturing processes used to produce lubricating greases in that the regulatory bodies no longer allow the release of many different types of chemical components into the surrounding air and waterways and investments in equipment to prevent such contamination result in higher running costs for the producer. This has led to the use of chemical intermediates for the production of aluminium complex greases where no isopropyl alcohol is generated during the process and the introduction of the concept of using an ‘instant’ polyurea powder instead of having to handle toxic iso-cyanates and aromatic amines.

For the large volume of present-day grease, the lithium greases, additive technology has been at the heart of the development process. The use of lead is hardly an option any more and this has been replaced by many different combinations of chemical substances. Very few additive companies specialise in grease and the grease maker is often referred to the gear oil range. So the trend here has been towards sulphur–phosphorus technologies, often in combination with zinc. Zinc compounds, however, have also become a hot issue and there are, of course, new zinc-free greases to meet this demand. A recent trend has been the introduction of bismuth as a viable alternative to the old leaded products. Bismuth is, admittedly, a heavy metal but has been shown to lack the toxic properties of its previous counterpart.

New improved lubricating greases containing ash-free additives, the combination of lithium and calcium soaps to improve water resistance, the incorporation of functional polymers into the thickener matrix to improve 'spray-off' properties and many more customer-specific solutions have been offered. In the pipeline are products containing functional soaps, nano particles (nested spheres) and lyotropic liquid crystals. In scientific terms, the trend is moving from *know how* to *know why* as more is understood about the actual mechanisms involved in grease lubrication.

In an attempt to raise the upper temperature limit for lubricating greases, the development of so-called complex greases has resulted in a new generation of multipurpose products. The market share for this type of product has risen dramatically, especially in the United States, but Europe is not far behind. In many cases, however, the higher temperature performance has been achieved at the cost of a deteriorated lubricating ability at more normal temperatures and this has resulted in problems with 'dry running' under ambient conditions. A clear increase in the use of lithium complex products has been seen at the expense of more conventional lithium products. Other solutions have been introduced but they have not really shown any significant market development over the past 5–10 years. Aluminium and calcium complexes, calcium sulphonate complexes, and even polyureas have all taken a small market share but quickly flattened out at low percentages of the total market. The introduction of synthetic fluids has also increased in parallel to the increased demands from OEMs and high-technology industries. Most of these can raise the upper temperature limit somewhat compared to mineral oil-based products but this effect is often grossly overestimated. The real advantage of synthetics is at the other end, at low temperatures, and where there are special demands on service life, low friction under heavy loads or energy savings in critical machine components.

The demand for more environmentally friendly products is always a major point of discussion but this rarely results in any real commercial sales. This will, however, change dramatically in the not-too-distant future when the different authorities will start implementing the new regulations and legislations, especially within the 'new expanded' European Union. This can clearly be seen already in the North Sea basin where certain products and chemical substances are now quite simply forbidden. The use of metallic surface separators in thread compounds is an illustrative example where such materials are no longer allowed. The EU has also issued the so-called Dangerous Preparations Directive and this has had a significant impact on the labelling of lubricating greases and, hopefully a trend towards using products which fulfil the non-labelling status of that Directive. The implementation of the European REACH legislations, starting in 2005, as a first step in a global harmonisation programme, will further strengthen this effect. In addition, in December 2004, the European Commission issued new guidelines for a pan-European ECO-label. An increased demand has also been identified for products conforming to the new NSF listings for food grade applications [32]. All the old American regulations and approvals have now expired and all products, both old and new, will be classified according to new and different criteria and many of the existing greases will lose their food grade status.

Looking forward into the next decade, the need for more advanced science in grease technology is essential. The design of special components is becoming increasingly complicated and machines are becoming much smaller and lighter in weight and are required to run faster and withstand heavier loads. To be able to develop the optimal lubricants for these new conditions, the mechanism behind grease lubrication must be further studied and understood. There will be an increased specialisation in both products and markets and the survival of individual lubricants companies will depend on their ability to adapt to changing conditions. Not only new machines but also new materials will affect the development of greases. Plastics and ceramics are already common in designs and newer nonconventional lubricants are being developed to meet the technical requirements and the increasing demands about health and the natural environment.

14.6 Conclusions

The new image for the development of lubricating grease in this 21st century must abandon the concept of a cheap and relatively simple commodity. Grease is an exceptionally complex product incorporating a high degree of technology in chemistry, physics, rheology, tribology and the environmental sciences. It is a *basic machine component*, just as important as any other part of the machine and should be considered right from the start of any development project.

The 'art' of grease technology has become a complicated science. The dilemma facing the grease trade is that 'art is often much more profitable than science' [33].

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Part IV
Performance

Chapter 15
Lubricants and Their Environmental Impact

C.I. Betton

Abstract Environmental considerations have increased in importance in the last two decades and lubricants are part of that. The REACH Regulations apply to the components of lubricants. About 50% of a lubricant can be reclaimed using refining processes ranging from acid/clay treatment through to distillation/hydrogenation to produce up to Gp. II quality re-refined base oils. The major possible contaminants are the PAHs, which are effectively removed by optimised distillation/hydrogenation, metals, remnants of VI improvers, water and untreated acids. Sulphur contents of these base oils must be viewed differently from those of virgin mineral base oils. Certain PAHs are recognised carcinogens and pose a health and safety risk and must be controlled. The use of re-refined base oils is driven by the concept of 'sustainability', to minimise pollution and maximise the use of resources.

15.1 Introduction

15.1.1 A New Regulatory Framework

When the first edition of this book was published in 1992, the world was a very different place. Inclusion of a chapter on the environmental impact of lubricants was a fairly radical idea for the time but it did receive favourable comment from reviewers – as much for the fact that it was there, rather than commenting specifically on the content. An expansion of the environmental chapter to include the latest updates in research for the second edition in 1997, some of which was initiated during work with a major lubricant company, highlighted the actual environmental impacts of 'lost' automotive lubricants and identified the actual toxic compounds that affected certain species in the receiving ecosystems. This work had a fundamental impact on the design of roadways and the treatment of run-off, the first beneficiary being an upgrade of a major road in the southwest of the United Kingdom, the A30 trunk road across Dartmoor, a sensitive environmental area. Roadway run-off was no longer considered as being just rainwater and it was recognized that some

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treatment was necessary, particularly in pristine environments, before the run-off water could be diverted into a receiving river or stream.

In 1992 the concept of global warming and climate change was the preserve of the few and politicians were adamant that nothing should be done that could upset the ‘Great Car Based Economy’: a view that still prevails in some areas of the world but one that no longer represents the consensus view of scientists and a majority of politicians.

The change in the global understanding that actions have environmental consequences and that perhaps those consequences may not be acceptable has resulted in a change in the regulatory climate, nowhere more dramatically than in the countries of the European Union. On 27 February 2001 the European Commission issued a White Paper on a strategy for a future chemicals policy, setting out on a detailed consultation process that has culminated in the most radical and revolutionary change in the legislative control of chemicals in the world. The result of the consultation is legislation known as the REACH Regulation, standing for the Registration, Evaluation and Authorization of Chemicals, which reverses the emphasis of all previous chemical regulation and will fundamentally alter the ways in which any chemical is manufactured and used [1].

REACH is a Regulation that has come a long way in a short time. From conception, beginning with consultation in 2001, to the final agreement between Council, Commission and Parliament in November 2006 and the birth of the regulation in 2007, it is remarkable for so radical a change in the Law. REACH is both very simple in concept and very complex in detail. The regulation itself is nearly 1300 pages long, a daunting prospect at first but on closer examination the majority of those pages are in fact found to comprise methods for the determination of physico-chemical data, toxicological and environmental properties, methods that are already in operation under existing legislation. The simple fact is that REACH will replace over 40 existing EU Directives so that the overall change in the volume of regulations that companies, and all those who work with chemicals, have to come to terms with will be small.

The revolutionary aspects of REACH that affect all aspects of lubricants and their use reside in the fact that:

- REACH incorporates the ‘precautionary principle’ into the fundamental assessment of all chemicals,
- responsibility for demonstrating that a chemical can be used safely and without adverse impact resides with the manufacturer or, in the case of a chemical imported from outside the EU, the importer,
- the manufacturer must conduct a risk assessment that shows that the benefits of use will outweigh any adverse health or environmental impacts,
- the risk assessment must consider all aspects of the life cycle in the use of a chemical, from manufacture, transport and use to ultimate disposal,
- the burden of proof that a chemical is safe to use now rests with the manufacturer, rather than for the authorities to prove that a chemical needs to be regulated.

All of these must be demonstrated before a new chemical can be granted approval for sale and will apply to all chemicals currently on sale within the next 11 years.

What does this mean for lubricants? As discussed in detail below, a large portion of the lubricants sold are ‘lost’ during use. This, under the terms of the new regulation, means that it is a foreseeable use that lubricants that are sold will enter the environment. Consequently, the manufacturers of chemicals that are used in lubricants will have to provide information on the ecotoxicological properties of their chemicals. The manufacturers of the lubricants will need to ensure that the uses and impacts of the products are known and understood and that a risk assessment is made that will enable the products to be manufactured and used.

In the past the environmental impact of lubricants has been considered only in terms of the recycling of lubricant at the end of its useful life, but henceforth, all impacts must be known and understood and the benefits of using chemicals must be demonstrable and significantly outweigh any adverse consequences in terms of a cost–benefit analysis. A sound health and environmental performance will really be, at least in Europe, a prerequisite for continued operation.

15.1.2 Introduction to Lubricants in the Environment

In 1985 a report by the European Oil Companies Organisation, CONCAWE [2], showed that, of the total lubricant sold in the EU, over half was ‘consumed’ whilst some was recycled or burned as fuel. Table 15.1 shows the total lubricant production sold and then broken down into their ultimate, subsequent destinations. A breakdown of lubricating oil sales for the United States during 1981 showed that automotive engine oils represent the major component of total sales [3].

The total percentage of lubricant that is ‘successfully disposed of’ is that which is either recycled or burned, as 32% in Table 15.1. The major proportions of lubricant enter the environment in one way or another, mainly due to lubricant use, i.e. ‘consumption’. As far as automotive engine oils are concerned, the results of this consumption can be seen on motorways, roads and car parks as a black deposit of

Table 15.1 Total EU lubricant production and disposal

Category	Tonnes/yr × 10^3	Percentage
Total EU lubricant sales	4300	100
Consumed	2300	50–55
Recycled	700	15
Burned as fuel	750	17
Unaccounted for	600	13
Poured down drain deliberately	100	2

oil. Since this data was compiled, the total amount has changed only slightly but the recycled percentage has increased as a result of both the business advantage of recycling due to the increasing price of crude oil and the percentage burned as fuel being drastically restricted by the removal of the fuel rebate together with severe environmental restrictions.

Some lubricants are intended for use such that they are ‘lost to the environment’, examples being two-stroke engine oils, greases and oils used on railways, chainsaw bar lubricants, rubber oils used in tyres, many white oils and so on. Conversely, provided efficient management systems are in place, many industrial oils should be largely contained and thus should not escape into the environment. Accidents, however, inevitably occur and cause the environmental release of almost any and all types of lubricants. A gearbox seal that fails, high-pressure hydraulic lines that fracture and metal parts coated in residual oils all contribute to the ‘consumption’ of lubricants and add to the environmental burden. In Western Europe alone, the total amount of lubricant that enters the environment can be said to be roughly the equivalent of 12 oil tankers or one ‘Exxon Valdez’ per month.

Three major aspects of the environmental aspects of lubricants can be addressed:

(i) control, via engineering to minimise losses,
(ii) minimising the impact of these losses,
(iii) efficient collection and treatment of waste materials.

In terms of the lubricant, (i) is largely a matter for the equipment designer and builder. The specialist lubricant company is affected by (iii) and can affect (ii). The collection and treatment of waste lubricants will now be described and followed by consideration of the environmental impact of lubricants. Finally, the results of recent research into the impact of lost or ‘consumed’ automotive engine oils will be described.

15.2 Collection of Waste Lubricant

15.2.1 Introduction to EU Legislation

The EU legislation, as ‘The Waste Oil Directive’ [4], requires that the use of collected waste lubricants should be reclaimed as the major priority, rather than be burned as fuel. The withdrawal of the $40/tonne subsidy changed the emphasis towards reclamation and recycling. With modern reclamation plants and a shortage of base stocks as crude oil and fuel prices continue their inexorable rise due to increasing demands; this requirement continues to meet commercial demands. There is however a strong possibility that the Waste Oil Directive may be repealed, and the choice of whether to reclaim the oil is expected to revert to individual member state legislative control. Some lubricants, such as industrial oils, can be treated relatively easily and recycled, whereas others such as automotive engine oils require more sophisticated treatment to provide reusable base fluids of acceptable quality.

15.2.2 Used Industrial Lubricants

There are many potential sources of used industrial products but reprocessing is not an option for a large number of these synthetic- and fatty oil-based products. Some products, such as transformer and hydraulic oils, can be readily collected from large industrial concerns, suitably segregated and consequently contamination can be avoided. These oils may be regenerated to a recognised standard and returned to the original source.

15.2.3 Used Automotive Lubricants

These will include mono- and multi-grade crankcase oils from petrol and diesel engines, together with gear oils and transmission fluids. Used industrial lubricants that have been inadequately segregated will also be included. Apart from the degradation products from the in-service use of the oil, a wide range of contamination is possible, including the following:

- water, as a combustion by-product, rain water/salt water ingress,
- fuels, as residual components of petrol/gasoline and diesel fuels,
- solids, as soot, additives and wear metals, rust and dirt, etc.,
- chemicals, as used oil can be used as an unauthorised means of hazardous waste disposal,
- industrial oils, arising from inadequate segregation of oil types can allow contamination by fatty or naphthenic products.

There are many potential sources of used automotive oils, for example, DIY motorists, service stations, company car or truck fleets and waste oil collection sites. There is also an equally wide range of commercial collectors. Good management of a used oil collection system is paramount to minimise both the variability of the material supplied to a re-refining plant and the problems of contamination by toxic or hazardous materials. Worldwide legislation is increasingly controlling the collection and disposal of all waste materials, including used lubricants. As an example, large-scale, >3 m^3, waste oil collection vessels at service stations must now be licensed in the United Kingdom, as must also be any contractor who transports or treats waste lubricants [5]. Essentially similar legislation has been enacted in other developed countries.

15.3 Treatment of Collected Lubricant

15.3.1 Introduction to Used Lubricant Treatment

Simple initial processing such as gravity settling in storage and filtration/centrifuging is sufficient to remove coarse solids and water. A mild chemical treatment such as washing with a caustic soda solution may also be used to reduce the concentration of other contaminants. Disposal of the waste products separated by these initial treatments must be done according to hazardous waste regulations.

Waste lubricant was used to increase the calorific value of coal used in electricity generator utility plants, aided by a government subsidy of $40/tonne. This subsidy has been withdrawn with the intention of emphasising used oil recycling instead. Used lubricant is a good source of energy, and also hydrocarbons, but contains contaminants which, when burned, can cause environmental and operational problems. The control of emissions is a central factor governing used oil as a fuel component in the United Kingdom. Provided that strict limits on emissions are met, the content of the fuel is immaterial. The policy emphasis on recycling waste lubricant has now overridden its use as a fuel supplement.

15.3.2 Reclamation of Lubricating Oils

Some specific types of industrial oils can be readily segregated at source and are suitable for relatively simple reprocessing before being returned to their original service. Typical processing methods involve filtration and then removal of water or volatile decomposition products under vacuum.

Large-scale industrial users can arrange for on-site processing, such as the reconditioning of transformer oils at power generation plants, or can collect specific drain lubricants for offsite processing and return, such as the reclamation of railway diesel engine lubricants. These examples of customer-specific reprocessing can be cost effective compared to the expense of new oils and lubricants.

15.3.3 Production of Re-Refined Lubricant Base Oils

Complex processes are required to deal with the wide range of contaminants and additives present in waste lubricants from multiple sources. The objective is to recycle waste lubricants to produce base oils that can then be used as substitutes or alternatives to virgin mineral base oils. The main re-refining processes are summarised in the sub-sections below; most are continuous rather than batch processes and rely on receiving a reasonably homogenous used lubricant feedstock if the products are to be consistent.

One means of achieving consistency is to mix a month's supply of used lubricant and use that to feed a continuous process appropriate to the characteristics of the resultant mixed feedstock. There is a risk that contamination will spoil a large batch of feedstock and quality checks are very important.

Acid/clay Treatment: This was the original commercial process for reclamation of lubricant. The acid/clay process, such as the Meinken process, has the disadvantages that it generates large amounts of hazardous waste and cannot effectively remove the high concentrations of additives used in modern engine lubricant formulations. It is now superseded by other, newer, technologies.

In the acid/clay process, the used lubricant is first treated with 98% sulphuric acid to precipitate the suspended contaminants and additives. The resulting acid sludge is then separated and the remaining lubricant clay treated, neutralised and filtered. Process yields from modern used engine lubricants are low, of the order of 50–60% of the lubricant boiling range material, and large quantities of acid sludge and oil-soaked clay are produced. These wastes are both difficult and expensive to dispose of in an environmentally acceptable manner. Some applications have used a thermal pre-treatment to degrade some of the additives and reduce the workload on the acid treatment stage.

Base oils produced by the acid/clay process usually have a dark colour, have a ‘burnt’ odour and are inferior to virgin mineral base oils.

Solvent Extraction: Propane and other solvents can be used to selectively extract the base oil material from used lubricants, on the ‘like dissolves like’ principle, such as the IFP process. A high-boiling asphaltic residue containing most of the additives and other impurities is recovered as a separate stream. This is not the same process as the refinery furfural or phenol extraction which selectively removes aromatics by solvent extraction from lubricant base oil fractions.

Further finishing treatment of the separated base oil may be required but the initial process has been developed to give improved separation. Low-severity acid/clay treatment, clay treatment alone or hydrofinishing may be required.

Solvent extraction plants are expensive to construct and operate and also produce significant amounts of waste materials and hazardous by-products. Overall base oil yield, relative to the used lubricant input, is 70–80%.

Distillation/Clay Treatment: Thin-film distillation under high vacuum, such as Luwa evaporators, separates gas oil, lubricant oils and an asphaltic residue containing most of the additives and contaminants from the used lubricant feedstock. The lubricant base oil stream is ‘finished’ by clay treatment. Overall base oil yields are again 70–80% and significant amounts of spent clay must be disposed of.

Distillation/Hydrotreatment: This technology is the most recent development, as in the KTI and Mohawk processes. After pre-treatment and thin-film distillation, the base oil fraction is hydrotreated under moderate conditions. A final distillation step gives a range of base oil streams of different viscosities with process yields of up to 90–95%.

By-products are a low-boiling distillate, used as a fuel in the re-refining plant, gas oil and a non-hazardous waste asphaltic residue. Emissions and waste steams are limited, making this process capable of complying with very strict environmental controls.

Base oils produced by the distillation/hydrotreatment processes are of superior quality compared to the older, previously described, used lubricant recycling technologies. They can certainly be of Gp. I quality, in some cases Gp. I+, with some re-refining processors now claiming Gp. II quality standard with improved process technologies.

The distillation/hydrotreatment process is comparatively sophisticated, capital intensive and requires skilled operation, although operating costs are not exceptionally high. It appears to be the preferred process for the re-refining of used lubricants to produce high-quality base oils which can compete with virgin base oils at the Gp. I/II level.

15.4 Re-Refined Base Oil Quality

15.4.1 Introduction

Lubricant base oils must meet minimum performance characteristics of viscosity, viscosity index, pour point and volatility, all of which must meet required standards. When dealing with re-refined base oils, additional characteristics such as colour and odour must also be considered. These properties, of dark colour and odour, are readily perceived by customers and consumers as representing deficiencies in quality. Many examples of re-refined base oils have a definite, characteristic, ‘oxidised’ or ‘cracked’ odour which may be totally unacceptable in some countries and markets. Table 15.2 gives quality guidelines for the acceptance of re-refined 150 and 500 base oils.

Due to the variety of potential sources of used lubricants, their differing histories of service use and their subsequent levels of possible contaminants, assessment of the quality of the resulting re-refined base oil is a major concern. Quality assurance must be applied both to the used lubricant feedstock and, more particularly, to the product(s) of the re-refining process. Limits to the concentration of various contaminants in the finished base oil must be set and strictly adhered to.

15.4.2 Possible Contaminants in Re-Refined Base Oils

Fuel and Solvent Residues: These contaminants can be present in varying amounts depending upon the efficiency of the re-refining processes used. Flash point and Noack volatility values in excess of those in Table 15.2 indicate unacceptable contamination from these sources.

Polycyclic Aromatic Hydrocarbons (PAHs): These compounds are primarily present as a result of the combustion process during the previous use of the used lubricant prior to re-refining. PAHs are found at varying concentrations in used lubricants determined by factors such as drain interval, fuel type and sump size. Some PAHs are carcinogenic and the concentration of total PAHs in base fluids

Table 15.2 Guidelines for quality acceptance of re-refined base oils

	150 Grade	500 Grade
Viscosity at 100°C (cST)	5.0 ± 0.2	11.0 ± 0.4
Viscosity index	90–110	90–110
Flash point, PMC (°C)[a]	210	230
Pour point (°C)	–9	–9
Dialysis residue (%)[b]	0.1	0.1
Ring analysis, C_A (%)[b]	12	12
ASTM colour[b]	3	4.5
Total acid no.,(mg KOH/g)[b]	0.1	0.1
Noack volatility (% loss)[b]	18	6
IP 154 copper corrosion[b]	1	1
Odour	No foreign odour in finished product	
Chlorine (ppm)[b]	10	10
Water (ppm)[b]	50	50
PAHs (%)[b,c]	3	3
PAHs (ppm)[b,d]	250	250
Individual metal (ppm)[b]	10	10
Sulphated ash (%)[b]	0.01	0.01

[a]Mininum, [b]maximum, [c]by IP 246, [d]PAHs from fluoranthrene–coronene by Grimmer method

Data compiled by W.H. Preston and J.Z. Trocki

must be controlled. There is evidence that the distillation/hydrofinishing processes progressively and substantially remove PAHs as the used lubricant feedstock progresses through the treatment process. A more detailed discussion of PAHs is given in Section 15.5.

Metals: Metals should not be present in re-refined base oils either as wear metals, or from previous use of metal lubricant additives, or from the clay treatment or hydrofinishing catalyst fines. Metals are measured either by determining the total sulphated ash content or as individual metals by ICP analysis.

Non-Metallic Impurities: Viscosity index (VI) improvers or polychlorinated biphenyls, PCBs, can be determined by dialysis or chlorine analysis, respectively. Indication of the presence of VI improver is given by unusually high viscosity indices. Solvent extraction can remove VI improvers or their fragments.

Water and Untreated Acid: These contaminants maybe carried over from some processes. Total acid umber, TAN, and copper corrosion tests will indicate that these contaminants are present in the re-refined base oil.

Sulphur Content: This is seen as an index of inherent anti-oxidant capacity in virgin mineral base oils. For re-refined base oils, those hydrocarbons that were inherently oxidatively unstable would have been oxidised during previous use. The function of the sulphur content of a re-refined base oil is not clear and more work is required to determine the need or the concentration of sulphur required to meet minimum performance requirements.

15.5 Health and Safety Aspects of Re-Refined Base Oils

Used lubricants are recognised as posing a carcinogenic risk to humans. However, provided that suitable precautions are taken, such as good personal hygiene, the actual risks to health can be essentially eliminated. This is borne out by epidemiological studies on groups of mechanics where there has been no evidence of an increase in cancer.

The main carcinogenic agents in used lubricants are polycyclic aromatic hydrocarbons, PAHs, with 3–7 rings such as benz-α-pyrene, benz-α-anthracene and chrysene. These chemicals, and many others like them, are found in used lubricants, having been formed during the combustion cycle in the engine. PAHs are also present in crude oil and can also be present in unused base oil fluids leaving the refinery. Refinery technology is, however, able to remove these harmful PAHs by hydrogenation and solvent extraction. Strict limits of 3% on the dimethyl sulphoxide, DMSO, extract of virgin base oils have been introduced by the oil industry; these limits are based on animal studies which have shown that there is no evidence of carcinogenic activity at DMSO extract levels below 3% [2, 5]. It must be emphasised that the use of this method is valid only for virgin base oils produced from crude oil using 'conventional' refining techniques. Application of the 3% limit to re-refined oils cannot be relied upon as a demonstration of safety. Further assessment by experienced personnel is necessary for these types of fluids before any assurance of safety can be assumed.

PAHs are found in re-refined oil samples at a higher level than those found in unused base oil. A series of re-refined oils from different countries and different re-refining processes was analysed for PAH content by the Biochemisches Institut für Umweltcarcinogene in Hamburg; the results are given in Table 15.3. Interpretation of these results in relation to carcinogenic risk is not easy. The limits on total DMSO-extractable materials, taken as a measure of PAH content, in virgin base stocks were set based upon a knowledge of PAH distribution that is not applicable to the used oil situation. The probability is that re-refined base oils will present no significant risk to health, provided that normal precautionary measures of personal hygiene and handling are taken. However, until further biological studies are undertaken, the definitive position with regard to the carcinogenic potential of re-refined oils cannot be determined.

15.6 Environmental Considerations of Waste Lubricant

15.6.1 Disposal of Waste Lubricant as a Fuel

It is important to consider the total environmental costs and benefits of dealing with used lubricants. Previous sections have indicated that the quality of the re-refined product is determined by the nature of the feedstock and also by the treatment process. The total amount of energy consumed in the collection

Table 15.3 PAH analysis of re-refined oil

		PAH concentrations of oil sample, mg/kg (= ppm)								
Individual PAH	Virgin reference oil	1	2	3	4	5	6	7	8	9
Fluoranthrene	0.02	6.74	1.64	2.77	3.26	0.14	1.42	1.78	0.03	0.05
Pyrene	0.42	5.33	2.75	7.16	9.19	0.42	0.60	20.66	0.26	0.36
Benzo(*b*)naphtha(2,1-*d*)thiophene	0.34	0.89	1.02	2.29	0.60	0.07	1.24	0.38	0.04	0.03
Benzo(*ghi*)fluoranthrene + benzo(*c*)phenanthrene	0.01	1.02	0.11	0.37	0.21	0.12	0.19	0.29	0.03	0.04
Cyclopenta(*cd*)pyrene	<0.01	0.01	0.13	0.05	0.06	<0.01	0.11	0.08	<0.01	<0.01
Benz(*a*)anthracene	0.08	5.39	1.05	1.62	2.84	1.13	0.30	0.34	0.07	0.08
Chrysene + triphenylene	2.10	9.47	2.89	4.16	12.65	1.73	6.65	6.26	1.23	1.36
Benzofluoranthrenes (*b* + *j* + *k*)	0.28	6.84	0.98	1.20	12.32	4.37	2.43	4.93	4.53	5.36
Benzo(*e*)pyrene	0.41	3.56	1.04	1.41	14.46	6.28	0.65	6.51	11.3	11.2
Benzo(*a*)pyrene	0.01	0.83	0.53	0.60	1.65	2.82	0.13	0.31	0.47	0.47
Indeno(1,2,3-*cd*)pyrene	0.06	0.31	0.22	0.30	2.37	2.30	0.08	1.40	6.10	9.33
Dibenz(*a,h*)anthracene	<0.01	0.26	0.05	0.09	0.12	0.76	0.04	0.04	0.22	0.22
Benzo(*gh*i)perylene	0.53	1.63	0.86	1.14	5.05	11.49	0.40	5.97	38.5	36.3
Anthanthrene	0.03	0.12	0.09	0.21	0.11	0.16	0.11	0.08	0.6	0.6
Coronene	0.13	0.19	0.10	0.35	1.19	2.30	0.09	0.24	11.4	12.6
Known or suspect carcinogens measured	4.44	42.6	13.5	23.7	66.1	34.1	19.8	49.3	74.7	77.5
Total PAH content (3–7 rings)	7.5	87.3	22.6	52.5	93.5	49.5	30.2	112.0	67.7	126

Data compiled from results provided by the Biochemisches Institut fur Umweltcarcinogene, Hamburg and re-refining of used lubricants to an acceptable standard must be balanced against the energy to be gained from utilising the used material as a fuel. Clearly, the choice between no lubricant and an inferior base stock is also a major consideration.

Of the three basic methods of disposal of used lubricants, the most efficient in terms of energy conservation, in that it displaces an equivalent amount of oil, is the use of the material as a fuel or a fuel supplement. In heating processes where the fuel is supplied through a burner, some limited pre-treatment of the waste lubricants and blending with conventional fuels is necessary.

Pre-treatment can range from simple settling and filtration to heating, emulsion breaking, chemical treatment and centrifuging – the amount of treatment will depend on the nature of the used oil, the required fuel product specification and any requirements regarding emissions. The flue gas components of principal environmental concern are PCBs, PAHs, dioxins and heavy metals. Some treatment of the used lubricant will be required to ensure that emission standards for these are not exceeded when the waste lubricant is used as a fuel. Should this not be possible, the used lubricant must be considered to be a hazardous waste and treated accordingly. Waste lubricant can be successfully burned in boilers ranging in size from electricity-generating plants and industrial boilers to specially designed and produced small furnace and boiler installations. An EU limit of 1 MW has been set, below which it is not advisable to burn used lubricant oils. The tax rebate incentive of $40/tonne for burning waste lubricant oils as a minor addition to solid fuel has been removed by the UK government and boilers using it will require a specific authorisation under the UK Control of Pollution Act. However, the upward price of all oils may make removal of the tax rebate irrelevant.

One of the most satisfactory uses of waste lubricants is as a fuel extender in cement production, subject to control over metal content. The advantages of this disposal route are the low-cost, or free, calorific value of the waste as a fuel to the cement manufacturer and the wastes which might otherwise be vented to the atmosphere with the flue gases are retained within the cement product with no adverse environmental consequences. There are, of course, limits to the cement production capacity which can use this waste as a fuel, particularly as cement kilns are seen as the ideal disposal route for other hazardous wastes such as contaminated solvents. The capacity of cement plants to dispose of combustible wastes is also dependent upon the level of demand for cement, which reduces when the building industry is in recession.

15.6.2 Disposal as a Waste

Disposal of waste lubricant classified as a hazardous waste requires that it is burned in a suitably authorised incinerator at high temperatures to complete oxidation of the PAHs, PCBs and PCT (polychlorinated terphenyls). The expense of this disposal route is enhanced by the need to use additional fuel to maintain the high temperatures required. Such disposal is mandatory in many countries if the content of certain contaminants in the used lubricant exceeds predetermined concentrations, e.g. 20 ppm of PCB in Germany.

For re-refining, provided that the used lubricant is of a suitable quality and the process is able to generate a base oil product of sufficiently high quality, the principal environmental consideration concerns disposal of the re-refining process by-products. The effluents and waste products from some re-refining processes can be highly toxic and are either carcinogenic or a potentially serious hazard to the environment. If these by-product wastes are not disposed of correctly, they represent a potentially serious hazard to the environment which is at least as severe, and probably greater due to their concentrated nature, as that of the untreated waste lubricants. The cost of safe disposal of these wastes is high.

15.6.3 Re-Refining Energy Balances

The energy balances of the re-refining processes are important for their overall economic viability. The energy balance calculation in terms of the percentage weight feedstock for the three alternative disposal methods is:

- disposal as a toxic/hazardous waste – 0% energy gain with some additional energy input required to achieve and maintain high-temperature combustion. Net loss, X%,
- re-refining to produce base oils – net energy loss of 17%, assuming 70% recovery rate of base oil,
- use as fuel – net energy gain of 90–95%.

15.6.4 Use of Re-Refined Base Oils

The use of re-refined base oils to produce lubricants is increasingly considered on a worldwide basis. The driving force is the concept of 'sustainability' [6], in this application, the recycling of resources to minimise their environmental impact. These considerations, whilst commendable in principle, appear to ignore the environmental costs of collection and transport. Against this, the material must be collected for disposal in any case.

A modern re-refining plant producing a top-quality base oil is expensive to construct and is not common, therefore a comprehensive collection and transport system is needed to keep that plant supplied with used lubricant. Local solutions such as fuel use in correctly designed systems, if authorised, obviate the need for large-scale transport systems.

The benefits to be gained by conserving crude oil, as a non-renewable resource, by re-refining less than 1% of refinery output, must be weighed against the fuel and energy, as 90% of refinery output, used in transporting and processing the used lubricant to the re-refinery. It is also important that perceived environmental benefits must not take precedence over the quality of the resulting lubricant. A full life cycle analysis is required in each market to determine the true picture with regard to environmental impact. If lubricant quality is compromised, the results in terms of engine failure and loss of performance could lead to an overall environmental deficit when the cost of replacement parts and decreased efficiency are taken into account. The health consequences of increased PAH concentrations are also unknown and must be considered if re-refined base oils containing them are used.

Both quality and process control should be able to produce a product of known and consistent quality, suitable for use as a lubricant base stock. In past practice, however, oils that can meet the required performance characteristics have tended not to be readily available and have historically been expensive. For these reasons, the use of re-refined oils as a lubricant base oil was not considered to represent a viable alternative to virgin mineral base oils of consistent quality when these are readily available. More recently, the quality of re-refined base oils has increased to a high level, for some cases up to Gp. II quality, and in volume quantity. In addition, the substantially increased price of crude oil, and its associated products, has made re-refining of used lubricant much more economically viable. The alternative route of using the used lubricant as a fuel directly or as a fuel extender is now much more restricted and controlled by environmental legislative authorisations and is also much less viable economically.

15.7 Environmental Impact of ‘Consumed’ Lubricant

15.7.1 Constant, Low-Level Inputs

Research by the University of Sheffield, UK, measured the environmental impact of roadway run-off from a major UK motorway, the M1, at four separate sites.

UK motorway construction design collects all rainwater falling on the road surface at approximately 2000 m intervals and it is then fed via drainage channels into a nearby stream. This run-off is not treated in any way. This construction enables the effects of the lubricants and other contaminants lost from the traffic using the motorway to be studied by comparing the biology and chemistry of the receiving water downstream of the run-off entry point with the situation upstream. The sites studied were chosen in conjunction with the UK National Rivers Authority, NRA, and the Department of Transport, DoT, to be representative of receiving stream conditions, and as far as possible to determine, free of other sources of pollution. In this way the only factor affecting the streams was judged to be the run-off from the motorway.

The most striking feature of the studies was the minimal effect on the environment of the run-off. Of the seven streams initially surveyed, only one of those, that with the smallest natural flow of water, showed any effect on the biology of the system. This was measured by comparing the number and diversity of animals and plants in the area downstream of the motorway drainage input with those in the area immediately upstream. In the one affected area, the effects that were seen were basically a decrease in diversity, characterised by a decrease in sensitive species and an increase in those species typically resistant to the effects of pollution. Hydrocarbons typical of used engine lubricants were found in significant quantities in sediment taken from downstream sites, but not from upstream samples. Water samples were not found to contain any significant contamination. Laboratory samples, in which samples of contaminated sediment were extracted and separated into water-soluble (containing metals) and aliphatic, naphthenic and aromatic fractions, showed that the principal cause of toxicity was in the aromatic fraction. The other hydrocarbon components and, perhaps surprisingly, the metal-containing portions did not appear to have any significant toxic effect. More recent studies on behaviour have shown that the freshwater shrimp *Gammarus* avoids only those sediments contaminated with the aromatic fraction of the extract. Identification of the actual toxic components has revealed that the PCAs phenanthrene, pyrene and fluoranthrene account for up to 76% of the observed toxicity. These particular PAHs have been found not to possess any carcinogenic potential [3].

15.7.2 Large-Scale 'Catastrophic Inputs'

Following the Exxon Valdez incident in Alaska, the time and effort spent on clean-up was considerable. One of the most spectacularly effective means of treating contaminated beaches was the addition to the oil of nutrients that allowed the indigenous bacteria to degrade the oil in situ. Land farming and oxygen addition to contaminated soil have also proved successful in dealing with hydrocarbon contamination. Oil does biodegrade under aerobic conditions, albeit rather slowly. If a lubricant is subjected to one of the standard OECD tests for ready biodegradability, however, it will most probably fail to show more than 20–30% degradability. There are many reasons for this, perhaps the most obvious, yet most often ignored, is that the test was probably designed to assess a single water-soluble chemical, probably a surfactant, and not a complex mixture of poorly soluble hydrocarbons.

The environmental degradation of lubricating oils is less easily demonstrated. One of the problems is the complex and varied nature of the used material. Materials other than hydrocarbons can inhibit or influence the rate of degradation, which is of greatest interest. Once released into the environment, there is a finite time before the waste lubricant is bound up in sediments or soils. Once there, due to the hydrophobic nature of the material, water is excluded and conditions are essentially anoxic. Anaerobic degradation of oils does not readily occur in nature – much to the relief of the oil exploration and refining industry. However, waste lubricant on the road or in soil or sediments is not locked in place in the same way as crude oil in rock formations. Heavy rain can wash surfaces, churn up river beds and release sediments, whilst the action of animals and plant can oxygenate soils. One means of lessening the burden on the environment, and minimising the impact of ‘consumed’ lubricant, would be to use readily biodegradable lubricants.

Lubricants that are susceptible to microbial degradation were developed in the 1970s for use in outboard engines. These lubricants were based on synthetic esters, see Chapter 2, which are structurally similar to naturally occurring triglycerides, which increased their acceptability to the degrading organisms. More recently, lubricants based on rape-seed oil have been developed for use in chain saws and the hydraulic systems of vehicles such as snowmobiles which are used in environmentally sensitive areas. To develop a biodegradable lubricant, however, it is important to have a means of assessing biodegradability. This is by no means straightforward.

15.8 Biodegradation Tests for Oils

The concept of biodegradation is, at least superficially, a simple one. A compound is degraded by biological mechanisms and so is removed from the environment. The practice of biodegradability is less certain, however, as evidenced by the number and variation of the tests available. The relationship between test results and actual environmental persistence is well-established for some classes of compounds, for surfactants as an extensively investigated example. For the majority of other materials, however, no such link has been established.

All of the test methods currently used were designed mainly for use with single chemical species that have a demonstrable water solubility. Oils and oil products are mixtures of hundreds, sometimes thousands, of different chemicals which usually have low water solubilities. Whilst some existing methods can be used with materials of poor solubility, such applications are, at best, a poor compromise. In the following sub-sections, some of the main terms used in biodegradation tests are described. The differences between the commonly used test methods, and the difficulties of applying these methods to oil products are then outlined. Finally, an indication of the current applicability of test results to oil products is given.

15.8.1 Terminology: Biodegradation

Biodegradation is the breakdown of a chemical by organisms. This is considered at two levels:

(i) *primary biodegradation*, where the loss of one or more active groups renders the molecule inactive with respect to a particular function,
(ii) *ultimate degradation,* which refers to the complete breakdown to carbon dioxide, water and mineral salts such as phosphates, sulphates and nitrates, etc., which is known as *mineralisation.*

Ready biodegradability: ready biodegradability, or readily biodegradable, is an arbitrary definition whereby a compound achieves a ‘pass level’ in one of five named tests, either the OECD, Sturm, AFNOR, MITI or ‘closed bottle’.

Inherent biodegradability: Inherent biodegradability, or inherently biodegradable, is another arbitrary definition. In this case, a compound shows evidence of degradation in *any* test for biodegradability.

Biochemical oxygen demand, BOD: This term refers to the amount of oxygen consumed by microbes when metabolising or degrading a compound.

Theoretical oxygen demand, ThOD: The theoretical oxygen demand is the amount of oxygen required to completely oxidise a given chemical compound, calculated from its chemical formula.

Chemical oxygen demand, COD: Chemical oxygen demand refers to the amount of oxygen consumed during chemical oxidation with hot acid dichromate. It gives an indication of the oxidisable material present, but only as a second best to ThOD. Not all chemical compounds are oxidised by dichromate, particularly oil products and lubricants.

Dissolved organic carbon, DOC: This is the amount of carbon present in a test compound that is in aqueous solution.

Acclimatisation: Acclimatisation is the process by which microbes adapt and multiply to enable them to metabolise a compound with which they have not previously had any contact. This may take hours or weeks and, in some cases, may not happen at all, e.g., with DDT.

Inoculum: The inoculum is the mixture of bacteria and other organisms added to the test solution. The source of the inoculum can significantly affect the results of the test; increased bacterial numbers and previous exposure to similar materials can increase the likelihood of degradation occurring. Common sources of inoculums are river water, sea water, soil extract, sewage effluent, sewage sludge and activated sludge. Sewage-based inoculums can be obtained from works treating primarily either domestic or industrial effluent. Regulatory authorities stipulate effluent from a works treating primarily domestic sewage as the source of inoculums.

15.8.2 Current Test Method Variations

The purpose of any biodegradation test is to demonstrate a potential for a material to be degraded; it does not seek to show what will happen in the environment, indeed it cannot. The reason for this is quite simple; in a biodegradation test, the microbes utilise the test compound as an energy source and so degrade it. The test is set up so that all of the other nutrient requirements are met except for the carbon/energy source. The microbes, bacteria, fungi, etc., *must* utilise the test compound if they are to grow and it is this utilisation that is monitored, by measuring carbon dioxide evolution, oxygen depletion or DOC reduction. In the environment, there are many thousands of alternative energy sources available and there is no compulsion for the microbes to degrade the test compound, especially when other, ‘easier’, materials are available.

Five methods are currently available for determining ‘ready biodegradability’. These methods are OECD standard tests and are recognised by the European Union (EU), the United States Environmental Agency (US-EPA) and the International Standards Organisation (ISO). Table 15.4 lists the salient points of the five tests, each of which lasts for 28 days, in order of stringency, together with the CEC test for outboard two-stroke lubricants. The higher the concentration of test material, provided that it is not too toxic, and the greater the number of bacteria, then the greater the chance that some of the organisms in the test flask will be able to adapt to utilise the test material. Compounds that pass the MITI test, as an example, could easily fail a closed bottle test, yet both tests would enable a substance to be classed as readily biodegradable.

Table 15.4 Tests for determining ‘ready biodegradability’

Test method	Concentration of test substance, mg/l	Concentration of bacteria cells, cells/ml	Measures	Pass level, %	Test period, days
Closed bottle	2–10	250	O_2	60	28
OECD	5–40	5–250	DOC	70	28
Sturm[a]	10 and 20	10,000–200,000	CO_2	60	28
AFNOR[a]	40	500,000	DOC	70	28
MITI[a]	100	200,000	O_2	60	28
CEC	2500	1,000,000	C–H (by ir)	B	21

[a] These tests are being updated so that they will all use 1,000,000 cells/ml

[b] There is no ‘pass level’ for the CEC test, 70% has been adopted by some authorities, e.g., The Nordic Council

The choice of a ‘pass level’ is arbitrary. Reference materials in closed test systems, such as the five ‘ready biodegradability’ tests, do not show 100% removal, although most reference materials degrade to over 90% DOC removal. As the material is degraded and bacterial numbers increase, the concentration of the test material decreases. The law of diminishing returns begin to apply, and the threshold concentration for a material to be absorbed and metabolised can be passed such that it is no longer economical for the bacteria to metabolise the small amount of test substance remaining. Consequently, they ‘switch off’ their metabolic processes and become dormant. The accumulation of ‘stalling’ factors due to bacterial metabolism may also occur, preventing further growth. The concentration at which this occurs will differ on a case-by-case basis, but it is for this reason that it is practically impossible to demonstrate 100% degradability in short term tests. In many cases, the concept of 100% removal or complete degradation can only be shown in environmental simulation experiments using radio-labelled chemicals. Such an approach is not possible, however, with complex mixtures such as oils and formulated lubricants.

15.8.3 Problems with Lubricants

Aside from the insolubility of lubricants and the fact that the microbes responsible for degradation live in water, the complexity of the mixture referred to as ‘oil’ makes assessment in the existing standard tests difficult, particularly if the additives are considered as well.

Solubility: In natural systems, microbes produce emulsifiers that render insoluble matter accessible for degradation. All of the systems currently available were developed for water-soluble materials and, although the use of artificial solvents or emulsifiers is permitted in the test guidelines, their use is restricted to 100 ppm in tests related to ecotoxicology and product classification, and neither is permitted in the MITI test. This approach is, in most cases, ineffective with oils since much higher concentrations are needed to achieve solubility, which renders the conditions of the test doubtful.

Complexity: In assessing a single chemical, the analytical determination of concentration is relatively straightforward and the process of breakdown can be followed by the identification of metabolites. In a complex mixture of oil in water the amount of each individual hydrocarbon in aqueous solution varies according to the ratio of oil to water. As degradation proceeds this ratio changes; therefore, the pattern of hydrocarbons in aqueous solution changes. The ability of a single chemical, at a concentration representative of those used in the standard test methods, to induce acclimatisation in bacteria is well established. In a complex mixture, it is possible that not all of the individual components reach a concentration high enough to induce acclimatisation.

Residuals: With a pure compound, if 70% degradation is demonstrated, only 30% is left, which may be pure compound or metabolites – this may be determined analytically. With a complex mixture, such as an oil, if 70% is removed by degradation, what is the remaining 30%? It may be that all of the hydrocarbon is removed, leaving only the additives. It could be that 70% of everything has gone, leaving a 30% residue, similar to the situation with a pure compound. Using standard tests, it is not possible to demonstrate which parts of the product have been degraded.

15.8.4 Current Status and Applicability

The only oil product for which there is comprehensive data on environmental persistence is crude oil. The real environmental data has been generated as a result of the various oil spills that have occurred over the years. Such incidents have shown that crude oil does degrade. More recently, events in Alaska have shown that the addition of essential nutrients such phosphate, sulphate and nitrate, etc., can promote rapid degradation in a short time and at low temperature.

Given that existing standard tests were developed to correlate with the actual environmental situation for particular types of materials, surfactants, it can be seen that the application of existing test methods, where oil products invariably fail, to lubricants is not always appropriate. There is one test method, developed by the CEC for use with two-stroke outboard lubricants, as in Table 15.4, that does correlate with the environmental situation. Although a 67% pass level has been applied to this test, which correlates with environmental data for two-stroke outboard motor lubricants, some authorities require 70% to be in line with other methods measuring DOC. The CEC test was, for many years, a tentative test method and not an accepted standard. During this time, it gained widespread use and a degree of acceptance as a general test for oils. The reason that the test took so long to be accepted was that the degree of variation was not acceptable to the CEC, an organisation mainly concerned with engineering-type testing of fuels and lubricants. These deficiencies were eventually controlled to the satisfaction of the CEC such that the method was formally adopted for the evaluation of two-stroke outboard engine lubricants only in 1994.

There is a major problem with the CEC test which is now obsolete. This is because the method of measurement relies on extracting hydrocarbons from the test system using trichlorotrifluoroethane. This compound is subject to the Montreal Protocol concerning ozone-depleting substances and its sale has been prohibited since January 1995. Although it is possible to obtain a licence to continue using this solvent if it is deemed essential, the security of long-term supplies of a compound that can no longer be legally sold must be doubtful. In 2008 the CEC supported the formation of a voluntary working group (TDG-L-103) to update the obsolete method (CEC L-33-A-93).

There is a need, therefore, for an internationally recognised test for the biodegradation of oil products that will reflect the true environmental situation, i.e., given an adequate supply of nutrients and oxygen, microbiological degradation of oils can, and does, occur. The European oil companies, working through CONCAWE, set up a task force of bio-degradation experts to develop such a test. The salient points of the CONCAWE test are that it is based on the Sturm test with a significant difference in that it is performed in sealed serum vials, mixing being achieved by shaking. One-third of the vial volume is taken up by the test material/medium and inoculum and the remaining two-thirds volume being air. As the system is sealed, each vessel is sacrificed in order to make a measurement. This is achieved by adding alkali to the mixture, which converts carbon dioxide into dissolved inorganic carbon, which can be measured easily using standard laboratory equipment.

A major difference in the CONCAWE method is the use of a pre-exposed inoculums. All current standard tests, apart from the MITI test, specify an inoculum from a sewage works treating primarily domestic sewage. As these tests were developed for use with surfactants, this means that they effectively use a pre-adapted inoculum. This goes a long way to explaining the characteristically poor results obtained for oils in such tests. Work by the CONCAWE group showed that if the inoculum is pre-exposed for a period of two weeks then the degradation obtained is better than with a non-adapted inoculum. More importantly, the variability of results that is apparent when using inocula not only from different sources but also from the same source over time is greatly diminished. The CONCAWE test method has great promise for use with all poorly soluble mixtures such as oils and lubricants. It is now available as a draft test method, OECD 302D.

Until internationally recognised and accepted test methods that accurately reflect the environmental impact of oil and oil products are available, the oil industry will be obliged to work with current, limited, test methods. The inapplicability of these methods to complex mixtures of poorly soluble compounds must be understood for the apparent failures of oil products in biodegradation tests to be placed in their correct environmental perspective.

15.9 Performance

Lubricants are used in all aspects of manufacturing industry, transport and domestic life. The major factor affecting the globe at the present time is the contribution to global warming posed by the loss of greenhouse gases to the atmosphere. Industry (16.8%) and transport (14%) are significant sources of greenhouse gas emissions but are less than for power generation (21%). Other major sources of greenhouse gas emissions are beyond control by legislation or any other means. Intestinal gases (methane) from ruminants such as cows release large amounts to the atmosphere: the effectiveness of methane as a greenhouse gas is 21 times that of CO_2.

Irrespective of these comparisons, any improvements in the performance of industrial processes and transport will translate directly to reductions in the amount of greenhouse gases emitted.

In addition, the useful lifespan of lubricants is significantly greater than it was when the first edition of this book appeared 17 years ago. The oil change interval of a car engine was 3–6000 miles; now 10,000 miles or 1 year are standard, with some manufacturers recommending much longer intervals. Viscosity is also much lower than it was. ‘0W’ oils were unheard of but now are common. All of this means that the oil has to work harder to remain within specification for longer and longer periods, cutting down on waste and at the same time, sump size is reducing, with the actual volume of oil going down as the lifespan and technology goes up. All of these things confer environmental benefits. Performance is still key, not only for the motor manufacturer and the lubricant supplier but also for the environment.

As was mentioned earlier, however, it is not performance at any price, those days are gone. Tetraethyl lead was added to fuel as an anti-knock agent, with the lead emitted to atmosphere. With the awareness and regulatory controls that are now being put into place in Europe with REACH we can say with some confidence that were tetraethyl lead to be proposed as an anti-knock additive today, that it would not be allowed by the regulators.

This then is the challenge for the future. There will be a need for increasingly advanced lubricants and hence lubricant additives, they will be required to operate in harsher conditions, more effectively than in the past, and there will be no allowances made in the approval process for adverse health or environmental effects. Society has decided that it wants to have its cake and eat it, more is required from less and it will have to be paid for by the polluter, in this case by society and the user. This will present not only challenges to the lubricant manufacturer but also great opportunities to those who can deliver performance without pollution. The companies and development chemists who can deliver the ultimate high-performance lubricants that do not have adverse effects on health or the environment will reap the rewards of success. Those who do not will be consigned to history and the record books as examples of what industry used to be like in the bad old days, by our children and grandchildren.

15.10 Future Trends

As mentioned earlier, the largest proportion of lubricant enters the environment by virtue of its being used. Legislation has been introduced to reduce unauthorized disposal. Engineering has minimized leaks and has increased the dependence on service centres where computer-assisted diagnostics are required for the servicing of most modern vehicles, reducing the ability of the individual motorist to carry out any but the most rudimentary tasks in vehicle maintenance.

How will the additive components change in the future? Vegetable base oils are susceptible to oxidation by virtue of their double bond structures, although they are being used in some applications such as chain bar lubricants and two-stroke oils. It is possible to utilize vegetable oils in long use applications but the antioxidation protection needed is thus far excessive; however, the future utilization of the double bond to attach performance molecules to the base oil itself must be a long-term possibility.

Identification of the most environmentally acceptable (or more correctly, the least environmentally damaging) product is becoming not just desirable but with the onset of the REACH regulation, driven by law. It is the stated intention of the REACH regulation to promote the replacement of materials that are persistent, bioaccumulative or toxic by less harmful alternatives and it is a part of the final agreement of the text of REACH that where such chemicals exist at present, there must be research to identify less harmful alternatives.

There is an EU ecolabelling scheme that covers lubricants and it is possible to apply for the following products: hydraulic fluids, greases, chainsaw oils, two-stroke oils, concrete release agents and other total loss lubricants. The criteria for gaining the label are based on the low toxicity and biodegradability of the components as well as a requirement that the product is ‘fit for purpose’ but without a requirement that high-performance criteria are met. There are prohibitions of some ingredients.

If the ecolabelling scheme is extended to other types of lubricants such as engine oils, then there will need to be a recognition that different criteria, as far as prohibited substances, may be needed and that performance may be a major factor in contributing to environmental impact. ‘Fit for purpose’ may not be good enough. The aim must be to establish a level of performance that does not represent a deterioration in standards and to have a means for discriminating between products.

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Chapter 16
Oil Analysis and Condition Monitoring

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Abstract Lubricants are essential and expensive components of machine systems needing sampling, analysis and monitoring. Monitoring can be either performance testing or oil condition monitoring. Knowledge of the system's critical failure modes is essential for cost-effective oil and machinery monitoring. Contamination occurs by water, fuel, glycol, dirt, wrong oil, metal particulate, soot, oil degradation and additive depletion. Oil test methods include in situ or laboratory FT-IR, electronic particle counting, elemental metal measurement, X-ray fluorescence, viscosity, gas chromatography, water determination and RULER®. Condition monitoring data must be managed by storage, analysis and interpretation. Status levels must be established from the database and reported upon for individual and sequential runs of samples as condition indicators.

16.1 Introduction

16.1.1 Performance Monitoring Testing

Lubricants for machinery are complex products and require careful specification, procurement and lifecycle handling. Oil products are expensive machinery components that require monitoring and remedial maintenance to ensure reliability. Periodic sampling and testing are required to achieve the greatest usable life from in-service lubricants. Therefore some form of routine lubricant condition monitoring is a part of most equipment maintenance programmes. Effective equipment operation and maintenance management require early identification and warning of the initiation of an oil failure mode so that a remedy can be planned while minimizing production interference. Figure 16.1 illustrates the relationship between fault detection timing and maintenance costs [1].

In general, the cost of maintenance increases as the fault detection point advances, as in Fig. 16.1. The least cost occurs when the problem is a fluid fault. Early detection and repair of the source of the fluid fault prevents machinery damage and, if discovered early enough, the in-service oil may also be recovered by filtering or purification. By contrast, if the fluid fault is allowed to progress, the oil becomes

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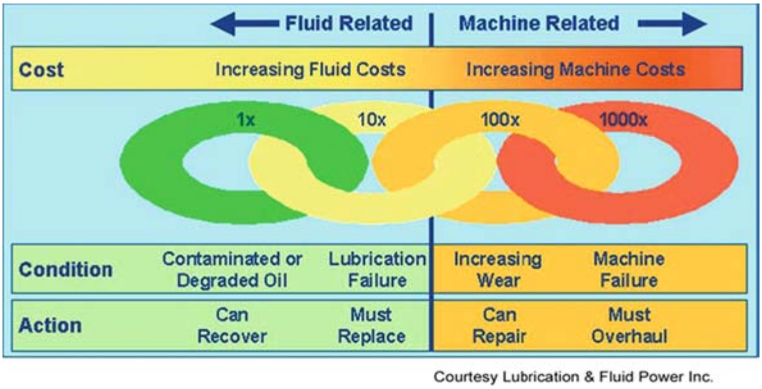


Fig. 16.1 Fault detection cost chain change, courtesy 'Lubrication & Fluid Power', courtesy GasTOPS Ltd.

depleted and results in damage to oil-washed components. At the end of the process, component damage accrues to the point of machine failure, dramatically increasing the cost of repair. Note that it is important to correct the root cause of the initial failure mode or the problem will occur again. Repeat cases of abnormal problems must be researched and solutions provided to remedy the root cause and minimize equipment lifecycle costs.

For in-service lubricant monitoring, there are two general approaches to lubricant analysis, either performance testing or oil condition monitoring. Performance testing, the subject of the next chapter, comprises a series of performance test methods developed to qualify new lubricants for use in specific machinery applications. Performance testing for in-service lubricants verifies the lubricant still meets specifications and is suitable for continued use until the next test interval. Performance testing is generally utilized to monitor in-service oils when there are:

- extended intervals between testing, such as in nuclear power plants; or,
- relatively large sumps, e.g., greater than 4000 l.

Traditionally, lubricant property (performance) test methods were used to determine in-service fluid condition. A variety of industrial organizations have standardized a number of physical test methods for this purpose. Utilizing lubricant property tests for condition monitoring introduces several physical and economic problems:

- each oil property has a respective test method that includes individual sample preparation, analytical procedure and provides only one parametric lubricant measurement.

- a large number of the common physical property tests expose the analyst to hazardous chemicals that also result in one or more waste streams that must be managed.
- these tests tend to be labour intensive and expensive.
- but more importantly, the results from the common lubricant property tests do not necessarily correlate directly with fluid failure modes. Thus, the results require manual interpretation before fluid condition is determined. In addition, abnormal lubricant property results do not easily translate into an identifiable root cause for the anomalies.

The complexity, time and cost of many lubricant property tests has meant that many equipment operators, particularly those with large fleets, rely on a partial oil condition assessment based on only one or two oil properties, for instance, viscosity and base number for diesel applications.

16.1.2 Condition Monitoring

Condition monitoring requires the measurement of the symptoms of the various fluid failure modes. The reliability of the fluid and equipment system is, or should be, the primary goal for an in-service oil analysis programme. Modern oil analysis programmes incorporate test instrumentation that can detect and quantify the individual symptoms of all oil faults that result in a functional loss of the fluid or component in the machinery [2]. The 1990s ushered in significant changes in the way oil condition and contamination testing are performed. Fourier transform infrared (FT-IR) spectroscopy provided the ability to quickly monitor multiple lubricant contamination and condition parameters with almost no operator training or hazardous chemicals [3–8]. This advance has been followed by the introduction of online/in-line sensors. These sensors range from monitoring wear metals [9, 10], to fine particulates [11], to oil condition and contamination [11, 12], utilizing a variety of measurement technologies. The advent of these technologies offers a wide variety of capabilities. It is important to note that condition monitoring is driven by an assessment of failure mode symptoms, not an assessment of oil properties or other parameters. An understanding of the systems' failure modes, symptoms and the means of their effective measurement is the key to success. The purpose of this chapter is to discuss these issues.

16.2 Oil Failure Modes

16.2.1 Introduction

Knowledge of the equipment system's critical failure modes is essential to cost-effective oil and machinery monitoring [13]. No equipment-monitoring programme should be established without clear knowledge of the critical failure modes including the:

- effects on the equipment and process,
- symptoms, at initiation, during mid-term and near endpoint (failure),
- intervals and data profile, from the initiation event through to failure,
- prevalence, how often do they occur and
- costs, in terms of maintenance required, lost production opportunity and cost to replace the lubricant or machinery components.

For machinery lubricating oils, the failure modes are well known and understood. They are generally characterized as either contamination or degradation related. Contamination faults occur when the oil becomes contaminated with liquid or solid materials such as water, fuel, antifreeze, insolubles (soot), ingress dirt or process materials.

Degradation faults occur as the oil is used in its service life. Oil additives degrade as a function of oil operational temperature, mechanical stress, age and contaminants. Oil usage and age introduce oil and additive breakdown by-products including the products of oxidation, nitration, sulphation and base stock breakdown. In addition, many oil contaminants can act as catalysts to increase the rate of oil degradation.

16.2.2 Water Contamination

Water is easily the most common contaminant found in machinery lubrication systems. For example, water causes 50% of bearing and power assembly failures in locomotive diesel engines (Table 16.1). Water contamination causes:

- breakdown of some lubricants, particularly esters,
- metal-on-metal contact and
- in the presence of metal catalysts, oxidation of the lubricant base stock.

There is a direct relationship between water contamination and component usable life. Table 16.2 shows the loss of bearing usable life as a function of water concentration [14]. Water usually enters an oil system as a consequence of condensation from environmental exposure, coolant leak due to a component failure or free water ingress during equipment cleaning.

Table 16.1 Locomotive engine problem audit

Major problem	Frequency	Percent of total (%)
Fuel leak	100	22.7
Coolant leak	220	50.0
Bad/incorrect oil	12	2.8
Ingress dirt	34	7.7
Main bearings	15	3.4
Con bearings	20	4.6
Power assemblies	35	7.6

Table 16.2 Water contamination effect on usable bearing life

Lubricant: SAE 20	
Water concentration (ppm)	Bearing life ratio
25	2.59
100	1.00
400	0.52

Courtesy Conoco-Phillips

Table 16.1 shows the reported contamination failure modes for medium speed railway diesel engines [2]. From a fleet of 1200 mainline locomotives, an average of about 320 contamination-related failure modes are detected and corrected each year.

16.2.3 Fuel Dilution

Fuel contamination is the second most serious contaminant in engine oils. In some diesel operations, fuel causes approximately 20% of engine failures (Table 16.1). Fuel contamination is usually the result of over fuelling, broken or defective fuel injectors, leaking high-pressure fuel lines, leaking oil/fuel heat exchangers, etc. Severe fuel leaks in medium speed diesel engines cause large decreases in the oil's viscosity, which in turn causes catastrophic damage to load-bearing components. For example, an experiment conducted by the Imperial Oil Co. at their Sarnia, Ontario Test Laboratory for the Canadian railway industry, revealed the extent of damage to locomotive diesel engines from fuel dilution. In the test of a Electromotive 645 medium speed test engine, 10% fuel dilution of the engine oil removed an average of 27% of the piston rings by weight in only 100 h of operation [15].

16.2.4 Glycol Contamination

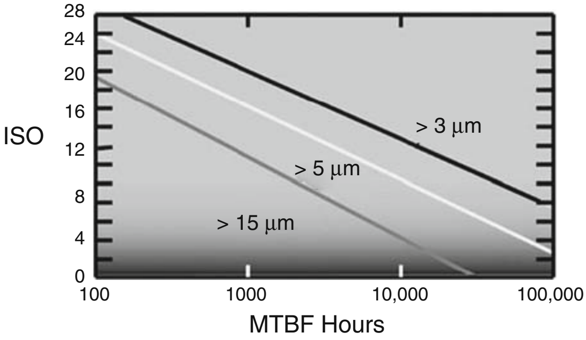
During cold temperature machinery operation, an ethylene glycol and water solution (antifreeze) is used for protection against cooling system freeze-up and component breakage. Glycol, a component of antifreeze, is a chemical solvent and reacts with the lubricant base stock and additive package, thickening the oil and accelerating oxidative degradation that leads to the formation of sludge and varnish. Sludge forms in the cooler parts of the engine and varnish on the hotter parts.

16.2.5 Dirt (Sand) Contamination

Close tolerance fluid systems such as hydraulic and oil-wetted anti-friction bearings require ultraclean fluids to prevent damage from hard particles entering the clearances between the working parts. Insoluble particulates due to dirt ingress and oil degradation increase with equipment usage. These materials cause silting, gumming and abrasion of machinery parts. As shown in Fig. 16.2, there is a direct relationship between oil cleanliness and component usable life, [16]. The graph shows the relationship between hydraulic system mean time between failure (MTBF) and the concentration and size distribution of ingress dirt particles.

The particulates of interest include hard sand, dirt and wear particles that are of the same size range as the machine oil clearances. The debris is generally in the range of 2–10 μm. These particulate sizes cause most damage and often result in component failure. For acceptable oil performance and reliability, particulates in the oil must be periodically measured, evaluated and when appropriate, removed by filtration.

Fig. 16.2 Dirt contamination, as ISO 1171/4406 values vs. machine MTBF



16.2.6 Wrong Oil Contamination

One of the most critical and often overlooked problems in oil condition monitoring is the introduction of an incorrect lubricant into machinery lubrication systems. Incorrect oil addition ranges from the introduction of foreign materials such as glycol or different base stock fluids to the introduction of similar oil of a different type or viscosity grade. Whilst incorrect oil is not a lubricant failure mode per se, it can be the root cause of real lubrication problems.

The use of oil types that are not approved and not suitable for the machinery application can result in lubrication failure, excessive wear and/or corrosion. The mixing of oil types that are individually approved for a specific use, but contain additives with different chemical constituents, can diminish the additive performance. In the worst cases, the additives may react with each other and precipitate out, resulting in lubricant failure, excessive wear and/or filter blinding/blocking.

16.2.7 Metal Particulates Contamination

Metallic particulates enter the lubricant as a consequence of the breakdown of oil-wetted surfaces due to ineffective lubrication, mechanical working, abrasion, erosion and/or corrosion. Metallic particles from deteriorating component surfaces are generally hard and increase the wear rate as their concentration in the oil increases. In addition, the presence of wear particles initiates abnormal wear in other components.

Some metals such as copper can act as oxidation catalysts and their presence increases the rate of oxidative degradation of the lubricant. Other metals such as zinc can be corrosive to silver machinery parts such as bearings and bushings. Determining the oil's metallic concentration, the accumulation rate and the sources of the individual metals is an important part of oil analysis.

16.2.8 Soot Contamination

Soot contamination is a common occurrence for in-service diesel engine oils. Soot generally results from piston ring blow-by from the combustion chamber or faulty seals. Soot contamination leads to varnish and sludge and also contains hard carbon particles that increase machinery wear. Detergent and dispersant additives function to clean machinery surfaces and hold soot particles in suspension, maximizing lubricant efficiency.

16.2.9 Petroleum Oil Degradation

In lubrication systems, organic compounds are exposed to high temperatures and stresses in the presence of oxygen and nitrogen (atmospheric air), resulting in the formation of partially oxidized and nitrated compounds. There are a wide variety of oxidation degradation by-products produced during machinery operation and the exact composition and distribution of these compounds are complex [17].

Because of environmental concerns over emissions and a desire to optimize the combustion performance, a correctly tuned combustion engine generates lower nitration than oxidation products. However, nitration products will develop in an engine that is mistuned usually when there is an excessive advance of the spark, for gasoline engines, or of the fuel injection for diesel engines [18].

The oxidation of trace sulphur compounds, sulphur-bearing additives or high sulphur fuels generates acidic sulphate by-products. The increase of oxidation and sulphation by-products generally results in an increase in oil viscosity and acidity levels. Over time, these by-products increase the production of varnishes and sludges and significantly degrade lubrication performance. Sulphate by-products escape into the lubrication system around piston rings and seals, building up over time.

Sulphur compounds are typically found in some mineral oils and may be added to fuel to serve as antioxidants and biocides for storage and as a lubricant for the fuel injection system. While environmental and transportation requirements have sharply decreased the levels of sulphur compounds in commercial diesel fuel, these compounds can still be found in some fuels intended for off-road or non-commercial applications.

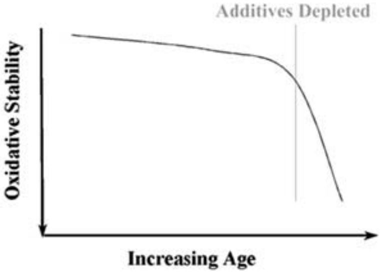
16.2.10 Polyol Ester Oil Degradation

Gas turbine engines can experience bearing failure as the result of lubricant starvation due to scavenge tube blockage by heavily ‘coked’ oil. The oil usually exhibits a blackened appearance and burnt odour. This form of degradation of polyol ester lubricants is due to excessive heat [19]. Overage or water contamination also cause the breakdown of the ester base stock. Typical breakdown by-products from ester degradation are a combination of alcohols and organic acids.

16.2.11 Additive Depletion

Most lubricant blends contain a variety of additives to improve lubrication performance for specific machinery applications. As the oil ages in a machine or is exposed to various contaminants, respective additives are consumed (Fig. 16.3). For instance, antioxidants serve to retard the degradation process. However as the additive is depleted, the rate of oxidation increases rapidly until complete lubricant failure occurs.

Fig. 16.3 Oxidative stability vs. additive depletion



In diesel lubricants, alkaline reserve neutralizes various oxidation by-products of combustion. However, as the alkaline reserve is consumed, by-product generation increases. Note that overbased detergents do not completely neutralize weak acids and thus allow acidic by-products to increase without a commensurate loss of base number, BN [20]. Determining oil condition based on remaining alkaline reserve, BN, alone is not recommended.

16.3 Oil Test Methods

16.3.1 Introduction to Oil Test Methods

In recent years, the available oil condition monitoring instruments and sensors have expanded greatly and are being continually upgraded and simplified. The requirements for an effective fluid condition monitoring programme have essentially been reduced to a set of three primary tests, augmented as necessary to generate specific diagnostics. The primary oil test methods have been selected to detect, measure and trend the relevant symptoms of the most critical oil failure modes. These tests generally fall into two categories:

- tests to monitor contamination-induced failure modes such as water, dirt, fuel, insolubles (soot), glycol (antifreeze) and any other process contaminant that may impact fluid cleanliness,
- tests to monitor oil degradation-induced failure modes caused by oil usage, temperature and age.

The tests utilized to measure these contaminants and degradation by-products include infrared (IR) spectroscopy, electronic particle counting (PC), Karl Fischer titration (KFT), atomic emission spectroscopy (AES) and X-ray fluorescence (XRF) spectroscopy. These methods are available in the form of off-line or at-line benchtop instruments and online/in-line sensors. Most off-line instruments are automated to provide several hundred analyses per day by a single technician. At-line instruments and sensors permit immediate results and diagnostic capabilities. Online sensors can be integrated into machinery control systems to provide real-time monitoring capability.

In general, all fluid measurement technologies must utilize effective analysis methods, performed at appropriate intervals whether sampled or online. However, what is effective? There are many different equipment-monitoring techniques and most can be justified on the basis of one technical reason or another. It is not always clear which technique is the most effective or economical. Nor do all the available techniques provide reliable or early indications of relevant critical failure modes. To be effective, the monitoring instruments or sensors must indicate the critical failure modes. Finally, the cost of using a particular technique must be considered. If the relevant critical failure mode symptoms are not properly measured and trended, the (lower) cost of the instrument or method becomes questionable.

The following sub-sections of this chapter are intended to provide a general overview of some of the common test methods used to determine lubricant condition and the presence and degree of common contaminants. It is important to remember that there are only a few oil-related failure modes that are critical to machinery operational reliability and these few symptoms require only a few of the available fluid tests.

16.3.2 Infrared (IR) Spectroscopy

The type and concentration of the molecules of many materials may be determined by their reaction to stimulation by infrared energy. IR spectroscopy measures the absorbance of light energy at specific wavelengths to identify and determine the concentration of specific molecules. When the frequency of an IR source is the same as the natural vibration frequency of a molecule, the incident IR energy is absorbed by the molecule causing the amplitude of its vibration to increase. The resulting vibration increase may be manifested as stretching, scissoring, wagging, rocking or twisting of molecular bonds. A natural consequence of these processes is that IR energy is lost (absorbed) at specific wavelengths, and this phenomenon may be utilized to determine the molecular structure and concentration. ASTM E2412 addresses infrared analysis of used lubricating fluids [21].

Dispersive Infrared Spectroscopy: The dispersive IR spectrometer generally incorporates an IR broadband source, sample cell, a diffraction grating and one or more IR detectors. Dispersive IR instruments may provide simultaneous or sequential measurements. Respectively, the instrument may have a fixed grating and many detectors, or a movable grating and a single detector. In some cases, the grating may be replaced by one or more optical filters to resolve the desired wavelengths. A reference cell and associated optics to perform simultaneous differential analysis are also incorporated to improve sensitivity or reliability of measurement.

Dispersive IRs are available as benchtop instruments or as online sensors. Online sensor systems are generally highly miniaturized and simplified versions of benchtop instruments. A typical sensor system will utilize one of the following configurations:

- a traditional dispersive spectrometer design that incorporates a solid-state source, a fixed diffraction grating and multiple IR detectors. Calibration is accomplished by electronic control over the source and detection circuits. In addition, the sample cell may be periodically moved out of position to emulate the action of the reference cell.
- an emulated dispersive design that utilizes bandpass filters rather than a grating to resolve detected wavelengths. These sensors are typically constructed by incorporating one of more sources, specific bandwidth filters and one or more detectors. These sensors may measure single or multiple oil analysis parameters depending on the number and bandwidth of the filters installed. Calibration is also accomplished by electronic control over the source and/or detection circuits.

Online sensors are designed to be installed in-line on operating machinery reservoirs using a partial flow fluid circuit. Oil is bled off the main oil system through the sensor and back to the reservoir or a dedicated ‘kidney-loop’ fluid circuit is provided. A filter is generally placed in front of the sensor to prevent large particles (dirt and metals) from damaging the integral transmission cell in the sensor. The oil condition sensor, shown in Fig. 16.4, is an example of a miniaturized version of an infrared spectrometer which includes an IR source, a transmission cell for the oil to flow through, a means to differentiate the spectral areas of interest, a detection system, signal conditioning and data interpretation electronics. This sensor is an example for online monitoring of lubrication oil developed within a project supported by the European Commission [22]. The sensor is solid-state and robust to withstand machinery fluid operating temperatures and the vibrations normally found in machinery operating environments.

Real-time, autonomous, fluid monitoring eliminates the need for sampling and remote laboratory analysis, thus providing timely data at reduced costs. IR sensors are already in service by the US military [23]. The sensors shown in Fig. 16.5 are a ferrous/non-ferrous metal sensor, a miniaturized dispersive IR spectrometer

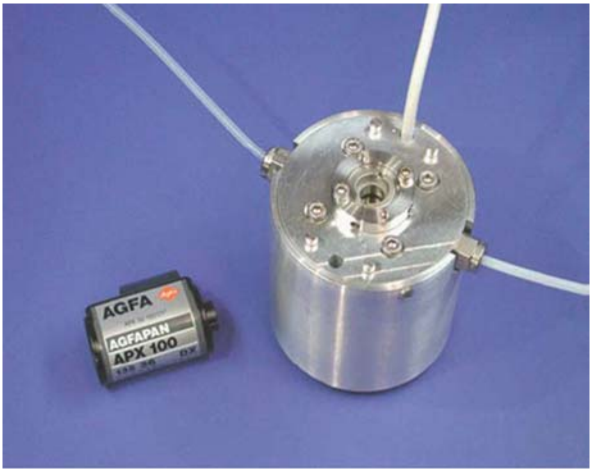


Fig. 16.4 Infrared sensor concept

Fig. 16.5 IR and metal sensor on USS Ramage DDG-61

and a viscometer. The IR sensor utilizes a transmission cell, a broadband infrared source, a diffraction grating, several IR filters and electronic detectors for each measured parameter. The sensor can be configured to determine oil acidity, water content, thermal-oxidative degradation, fuel/coolant dilution, soot loading and additive depletion.

Fourier Transform Infrared (FT-IR) Spectroscopy: With the introduction of commercial FT-IR spectrometers, the application of oil analysis by IR became relatively commonplace for production oil analysis laboratories. The mathematically intensive infrared data analysis techniques that were difficult or impossible to perform on the earlier IR systems became easy on these systems. In addition, quantitative analysis measurement techniques such as peak height, peak area, local baselines and more sophisticated matrix methods could be easily employed in the analysis, and the automation of lubricant analysis became commercially viable.

FT-IR uses a low power, broadband, infrared beam that is converted into a uniform pattern of constructive and destructive interference by a Michelson interferometer. The interference pattern is then passed through the oil sample, where it is altered by the characteristic absorbance bands of the various oil and contaminant molecules. The interference pattern finally enters a detector where it is converted into an audio frequency electronic signal. The audio signal is resolved into individual wavelength and amplitude data by a fast Fourier transform (FFT) software program. A single wavelength reference laser beam controls spectral bandwidth and measurement resolution. The laser beam passes through the interferometer to a detector. The detected sine wave signal from the laser determines the precise position and velocity of the moving mirror, data that are used to establish spectrometer bandwidth and resolution criteria.

IR Sample Introduction: The horizontal attenuated total reflectance (HATR) sampling technique offers a quick and simple analysis solution. However, the low infrared throughput of a HATR cell, coupled with its very short effective path length, approximately one micron, makes the HATR unsuitable for some types of lubricants. The 100-μm (0.1 mm) path length transmission cell is more versatile as it provides a high infrared throughput for a wide range of lubricants while amplifying the base oil bands 'off-scale'. In addition, the path length of the cell can be easily monitored from the fringe pattern generated by the empty cell. Resistance to polar contaminants, such as water, alcohols and glycols, is easily overcome with water insoluble window materials such as zinc selenide, ZnSe, cells that are also resistant to ion exchange problems from heavily 'nitrated' used oils.

As the spectra in Fig. 16.6 indicate, a HATR cell results in a loss of signal sensitivity of about a factor of 20 when compared to a 100-μm transmission cell. This signal loss hampers analysis of petroleum lubricants and prevents analysis of synthetic esters.

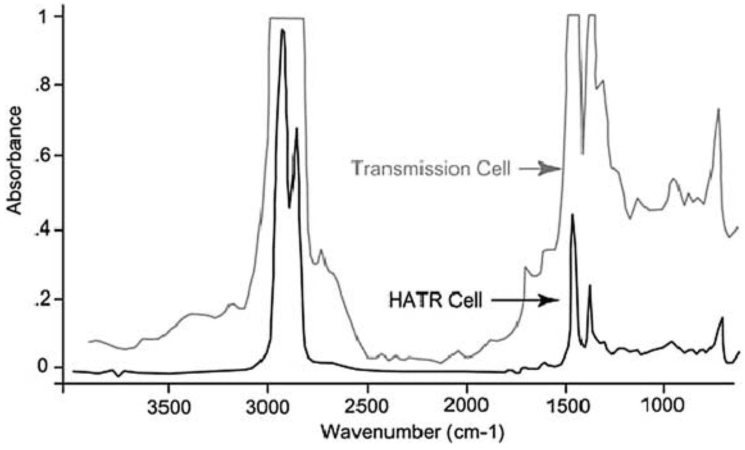


Fig. 16.6 HATR vs. transmission cell spectra

Data obtained using a HATR cell cannot be used for trend analyses with data from a 100-μm transmission cell and vice versa.

IR Analysis of In-Service Oils: The key to successful implementation of IR analysis for condition monitoring is the selection of appropriate areas to be measured and baseline points for each oil condition indicator for each lubricant type. Integrated area, as area under the curve, measurements are generally chosen over peak height measurements to improve data repeatability. Measurements must take into account the potential for baseline shifts due to changes in lubricant condition or contamination, e.g. baseline, spectral, shifts due to soot loading of an engine oil., otherwise the results may be masked or appear to be enhanced. Modern infrared quantitative analysis methods utilize local baseline points to eliminate the effects of spectral shifts. The individual organic compounds in the sample, e.g. the base stock, additives and contaminant properties, are quantified by measuring the absorbance at their respective wavelengths and generating representative scalar indicators, as absorbance values, for each data point. The use of specific oil analysis methods to automatically provide parametric data for each of the common oil failure modes eliminates the necessity for manual spectral analysis by an expert spectroscopist.

The IR spectra of the most common machinery lubricants are shown in Fig. 16.7. As can be seen, petroleum, polyol ester and phosphate ester fluids have different spectra. In addition, petroleum oils are broken down into detergent (crankcase) and non-detergent (bearing and gear) oils, which exhibit different responses to IR analysis. Thus, modern IR oil analysers and sensors will use multiple analysis methods to cover all required oil measurements for the lubricant types encountered.

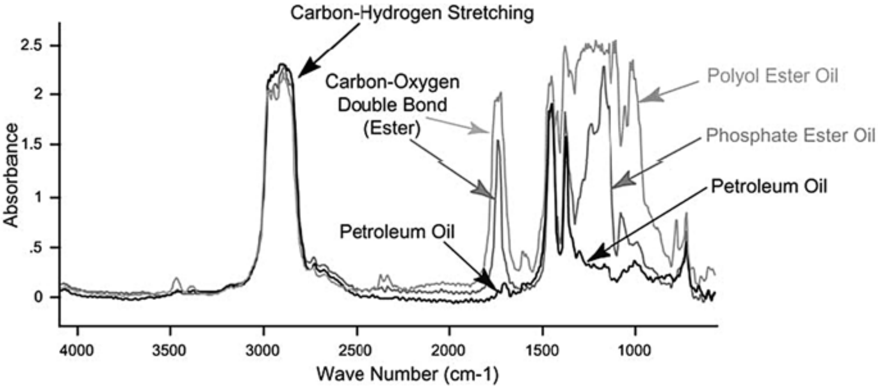


Fig. 16.7 Example of infrared spectra for common oil types

Water in Petroleum Engine Oils: Water is a very strong infrared absorber and perhaps the easiest to detect. The hydrogen-bonded O–H stretch vibrations (symmetric and asymmetric) of liquid water are found over the range of 3600–3150 cm^{-1} in petroleum-based lubricants. As there are few compounds found in petroleum-based oils that absorb a significant amount of energy in this region, a very general baseline over the range of 4000–2000 cm^{-1} will correct for the most common interferences such as soot, insolubles, dirt loading, unless the loading becomes so excessive that the amount of infrared energy passing through the sample drops to near zero. It should be understood that any contaminant loading of this magnitude is well beyond the normal operating range of the equipment and that alone will condemn the oil. Figure 16.8 clearly illustrates the incremental IR response of water for petroleum engine oils.

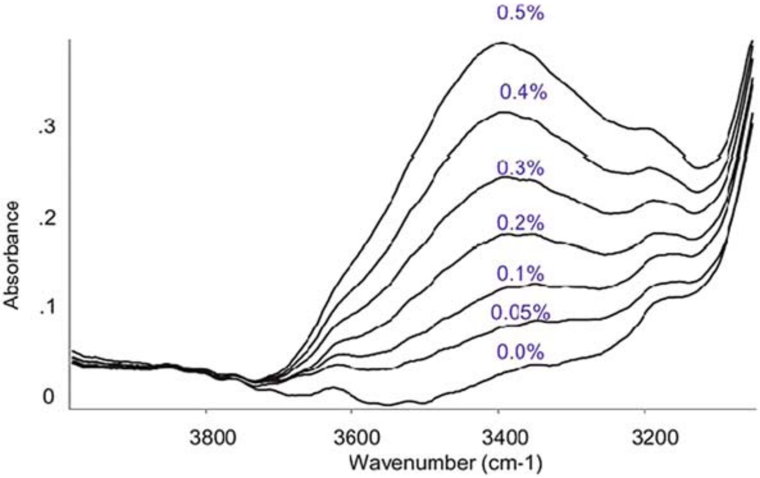


Fig. 16.8 IR response to water contamination in engine oils

Water in Polyol Ester Oils: The traditional hydrogen-bonded hydroxyl area, 3600–3150 cm^{-1}, was not successful for measuring water content in polyol ester, synthetic, lubricants. The spectra from prepared polyol ester samples indicate two peaks, at 3640 and 3550 cm^{-1}, corresponding to increases in water contamination (Fig. 16.9).

The 3700–3595 cm^{-1} region corresponds to free hydroxyl, i.e. no hydrogen bonding, and the region from 3595 to 3500 cm^{-1} corresponds to a single bridge hydroxyl group. These areas are not unexpected, considering the hindered structures of polyol ester oils. To correct for baseline offset and tilt from other components in used oil samples, a left baseline minimum is taken in the 4000–3680 cm^{-1} range and a right baseline minimum in the 2200–1800 cm^{-1} region. Only the region from 3700 to 3595 cm^{-1} is used for water contamination measurements. Note that in the FT-IR spectra shown in Fig. 16.10, both the petroleum, Mil-PRF-2104/NATO O-1236, and the synthetic, Mil-PRF-23699/NATO O-156, lubricants are contaminated with the same amount of water.

Water in Petroleum Steam Turbine Oils: As before, where water was observed to respond differently in high detergent/dispersant petroleum oils when compared to synthetic polyol ester oils, water also shows a different IR response in lubricants and hydraulic oils containing emulsifier additives. The response is typified by a constant

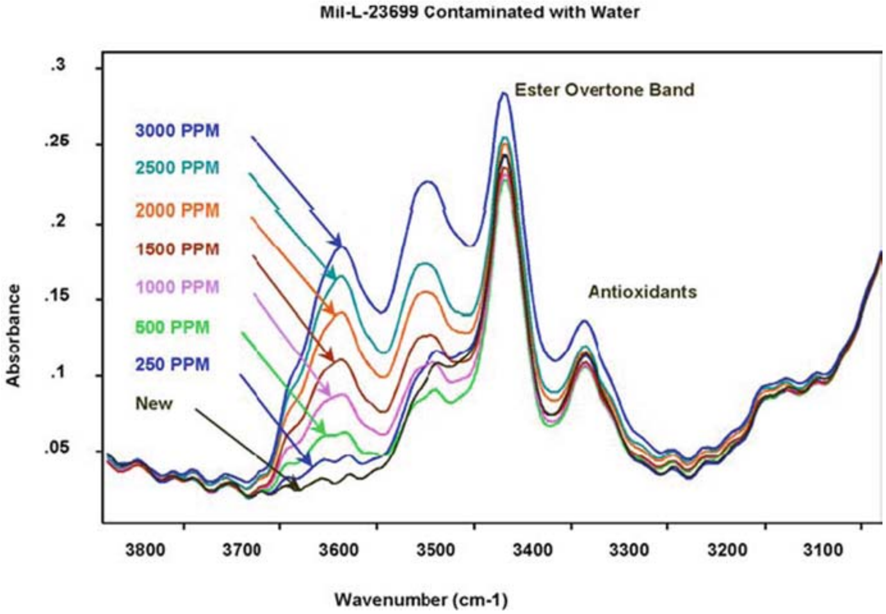


Fig. 16.9 IR response to water contamination of polyol ester turbine oil

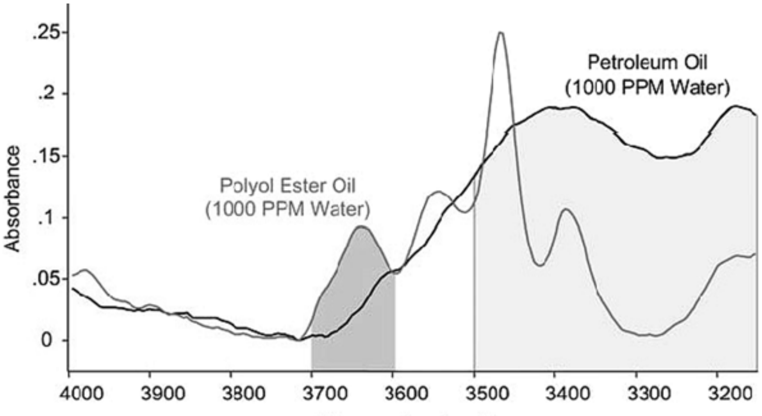


Fig. 16.10 1000 ppm (0.1%) water contamination in petroleum and polyol ester lubricants

baseline offset that is related to the quantity of water contamination (Fig. 16.11). The baseline offset due to water can be differentiated from the baseline shift due to particulate soot, as soot contamination results in offset and tilt. In addition, confusion between the two is unlikely, as soot is not a contaminant usually found in steam turbine lubricants.

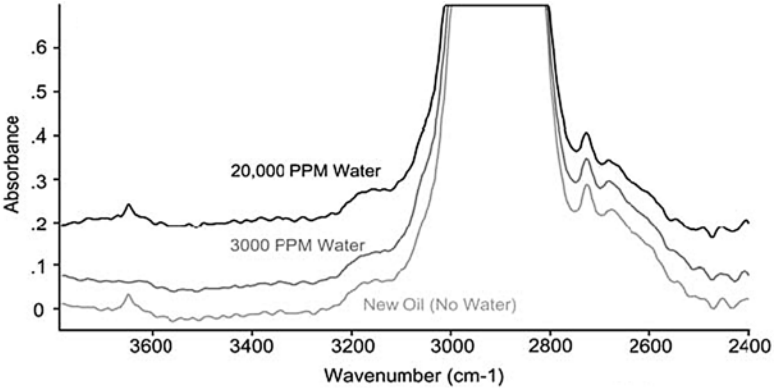


Fig. 16.11 IR response to water contamination of a steam turbine oil

Water in these oils is measured over the wavelength range of 3400–3250 cm^{-1} with no baseline correction applied. This range shows sensitivity to both the baseline shift due to low levels of water contamination and the hydrogen-bonded OH stretch response characteristic for higher levels of water contamination in these oils. The IR response for this lubricant class is insufficient to determine low levels of water contamination. Karl Fischer titration is recommended for low-level water determination for petroleum turbine and hydraulic oils.

Gasoline in Engine Oils: A band at 750 cm^{-1} identifies gasoline contamination. The most probable functional group producing a significant absorbance in this region is an out-of-plane bending of four adjacent hydrogens in an ortho-substituted aromatic ring. Whilst a single FT-IR band is insufficient to identify an exact compound, ortho-xylene is a common component in blended gasoline. Although there is an ASTM test method, D5580, for the determination of various aromatics in gasoline including ortho-xylene, the purpose of a condition monitoring method is not to determine or ‘reverse engineer’ the lubricant or fuel composition but to quickly monitor potential contamination.

Baseline points are taken as the minima between 780 and 760 cm^{-1} (left) and between 750 and 730 cm^{-1} (right), and the area is measured over the region 755–745 cm^{-1}.

Diesel and Jet Fuel in Engine Oils: Diesel fuel consists of different compounds, additives and reformates than gasoline. Marker bands typical of lubricants contaminated with diesel fuel are found around 810, 767, 740 and 700 cm^{-1}. The 810 cm^{-1} absorbance peak is generally the strongest and is often the only region used (Fig. 16.12). This peak is typical for out-of-plane bending of two adjacent hydrogens in a para-substituted aromatic ring. As the diesel fuel markers are also narrow, specific bands, restricted baselines are also used. Baseline points for the 810 cm^{-1} peak are taken as the minima between 835 and 825 cm^{-1} (left) and between 805 and 795 cm^{-1} (right). The area is measured over the range of 815–805 cm^{-1}.

Jet fuel is similar to diesel fuel and has a wide range of compositions and reformate levels. There are a variety of military and commercial jet fuels and the

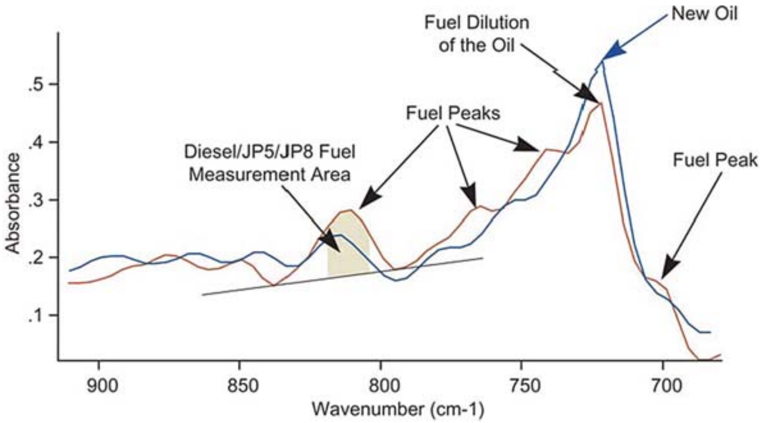


Fig. 16.12 Areas of interest for measurement of diesel fuel contamination

specific fuel used may be decided more by local availability than specific formulation requirements. Although jet fuels may vary in composition, they typically show the same infrared response as diesel fuel in a contaminated lubricant. For this reason, the diesel method described above is also used for the jet fuels JP5 and JP8.

It is important to note that some diesel and jet fuels have been formulated with little or no aromatic content. These fuels lack the 810 cm^{-1} marker band discussed above and alternate IR regions or alternate test methods must be used for fuel measurement.

Coolant Contamination in Engine Oils: Engine coolant is generally a mixture of water and ethylene glycol or water and corrosion inhibitors. The strongest absorbance bands from glycols can occur in the O–H stretch region. Water also absorbs in this region. The strongest, distinctive absorbance in glycols is from the C–O stretch doublet, located around 1080 cm^{-1} and 1040 cm^{-1}. While the absorbance pattern (or bands) from glycol in this region is very distinctive, other compounds from both additives and contaminants can contribute to the absorbance intensity in this area. To avoid contributions from other compounds, the characteristic glycol band area is measured over the region of 1100–1020 cm^{-1}, with two minima taken as the baseline correction points. The left baseline point is taken as the minimum over the region of 1130–1100 cm^{-1} and the right baseline point over the region of 1030–1010 cm^{-1}. Figure 16.13 shows three representative samples of in-service engine lubricants, one with no significant coolant contamination as a new oil, a second with some water and glycol contamination and a third with severe water and glycol, ~50/50, contamination.

Soot Contamination in Engine Oils: Soot is measured by the analysis of the baseline tilt at 2000 cm^{-1}. Figure 16.14 shows the varying IR spectral response as a consequence of low, intermediate and high soot concentrations. Note that the baseline tilt due to soot loading will affect any other parameter that is measured as a peak height from the minimum absorbance line, i.e. 0 Abs. In addition, high water concentrations have been observed to interfere with the measurement of soot by pushing

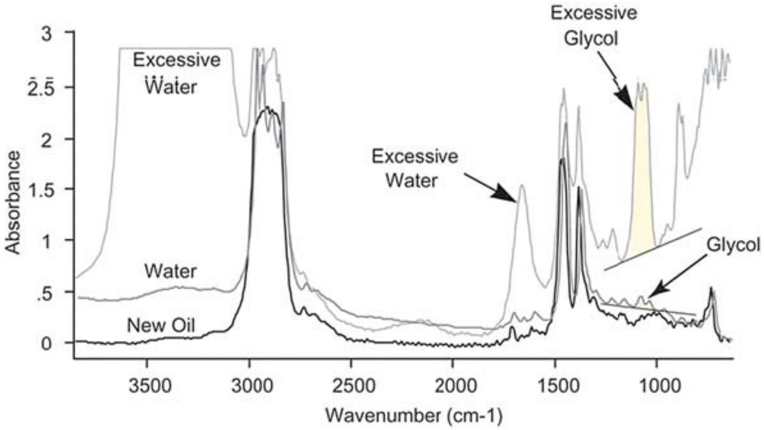


Fig. 16.13 Infrared spectra of glycol in motor oil

the soot measurement area higher. However, the interference does not become significant until the water level is on the order of between 40,000 and 50,000 ppm, 4–5%. This level of water would normally condemn the lubricant as unsuitable for use, regardless of the soot loading. However, even higher levels of water contamination are not uncommon in Northern European engine lubricants in winter as a consequence of repeated short journeys.

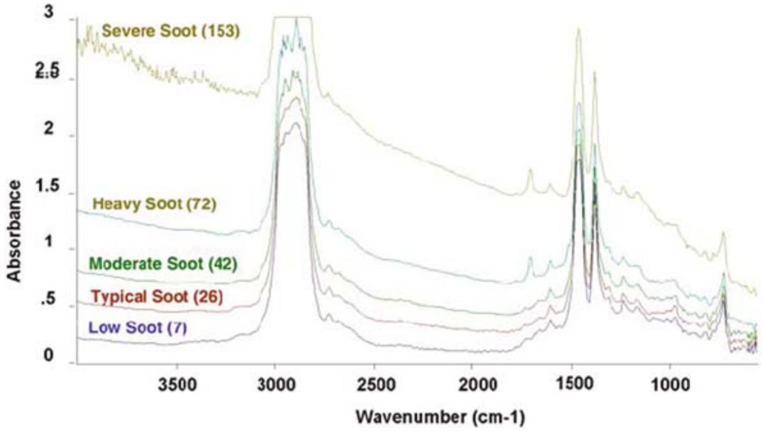


Fig. 16.14 Infrared spectra of soot loading in engine oil

Oxidation of Petroleum Oils: IR analysis determines the level of oxidation by-products in petroleum lubricants by a general response in the carbonyl region (Fig. 16.15). The infrared area is measured over the range of 1800–1670 cm^{-1} with two minima taken as the baseline correction points. The left baseline, high wave number side, is taken as the minimum over the region of 2200–2000 cm^{-1} and a right baseline, low wave number side, over the region of 600–550 cm^{-1}. This baseline definition corrects for any offset and tilt due to soot and particulates. Few compounds found in new and used petroleum lubricants have significant absorbance in these baseline areas. However, some additives have minor absorbencies in this region and will contribute to the overall intensity [21].

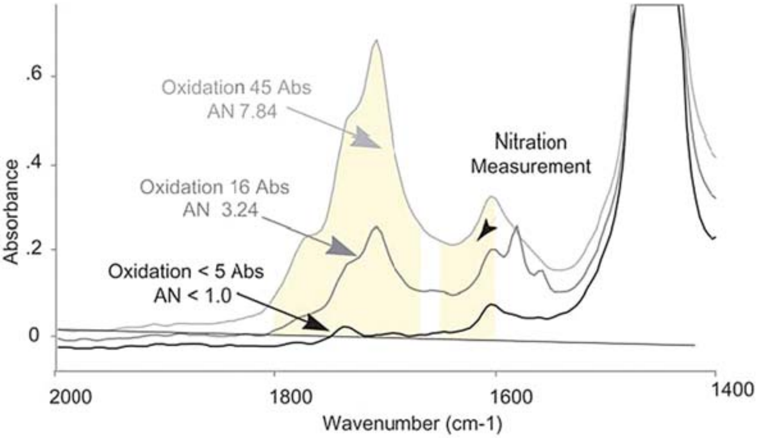


Fig. 16.15 Areas of interest for oxidation by-products in petroleum oil

Nitration of Petroleum Oils: Nitration by-products can be monitored by measuring the absorbance area from the NO_2 symmetric and asymmetric stretch over the range of 1650–1600 cm^{-1} (Fig. 16.16). The nitration measurement uses the same general baseline as the oxidation measurement.

Sulphation of Petroleum Oils: Sulphate by-products are measured over the region of 1180–1120 cm^{-1}, using the general oxidation baseline. Over this region, the most probable absorption group will be either from an SO_2 symmetric stretch or the SO_3 stretch from $C–SO_3–H_3O^+$. Figure 16.16 shows examples of used petroleum engine

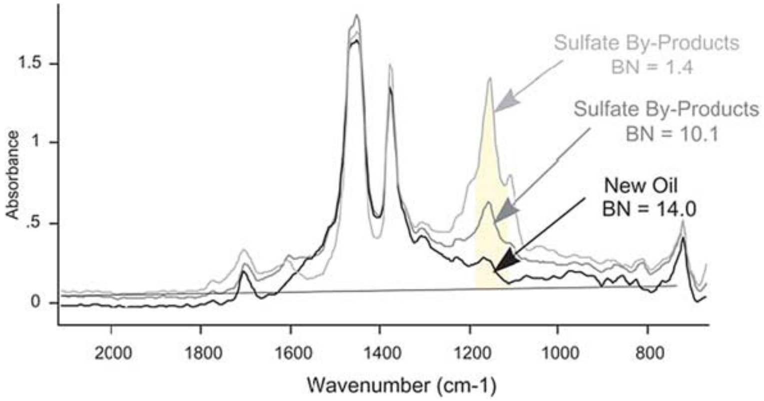


Fig. 16.16 Area of interest for sulphation by-products in petroleum oil

oil with excessive levels of sulphate by-products together with other contaminants. The first sample shows an excessive level of sulphate by-products and a corresponding excessive loss of alkaline reserve, indicated by the low, 1.4, BN measurement. The second sample shows a moderate sulphate reading with some decrease, 10.1, in BN. The third sample is a new oil with a BN of 14.

Breakdown of Ester Basestock Oils: Basestock breakdown in polyol ester lubricants is observed in two IR areas. Area I around 3535 cm^{-1} indicates that the breakdown products are mostly composed of weakly hydrogen-bonded alcohol or acid groups. Base stock degradation is measured over the range 3595–3500 cm^{-1}. A single baseline point for this measurement is taken at 3595 cm^{-1} to eliminate any interference from water contamination because as water contamination increases, the baseline shifts accordingly.

Breakdown area II is observed over the range of 3330–3150 cm^{-1} and is due to the numerous hydrogen-bonded by-products formed from the polyol ester lubricant breakdown. The left baseline, high wave number side, is taken as the minima in the region of 4000–3820 cm^{-1} and a right baseline, low wave number side, as the minima in the region of 2200–1800 cm^{-1} (Fig. 16.17).

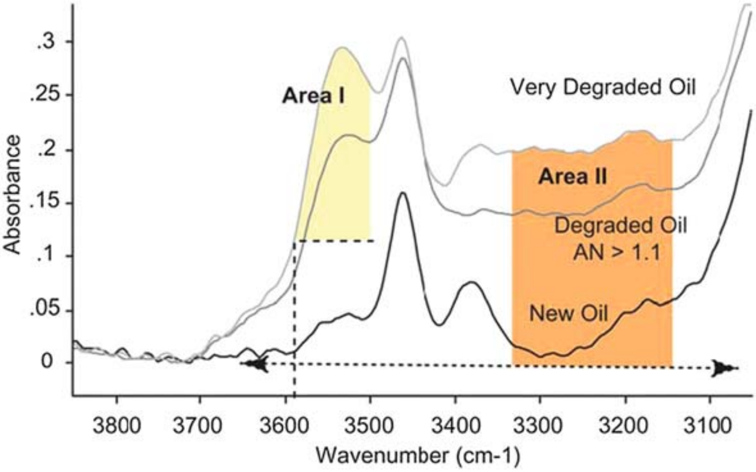


Fig. 16.17 Area of interest for breakdown by-products in polyol ester oil

Additive Loss in Lubricants: Additive loss is detrimental to the performance of lubricants. Some additive levels can be monitored by infrared spectroscopy. For instance, anti-wear additives, zinc dithio-dialkyl (diaryl) phosphate (ZDDP) and tricresyl phosphate (TCP) contain a common phosphate functional group that can be measured by infrared. The P–O–R (where R = alkyl/aryl) stretch shows a strong IR absorbance for all of these compounds and is used to trend the anti-wear level. The P–O–R stretch area is measured over the region of 1020–960 cm^{-1}, using the general baseline of 2000–600 cm^{-1}.

Under normal machine-operating conditions, oxidation begins to degrade the lubricant resulting in sludge and deposit formation, filter blockages, oil thickening, and an increase in oil acidity. Antioxidant compounds are added to lubricants to improve fluid performance in high stress or long life applications. Antioxidants are specially formulated for each machine type and service, considering the potential for exposure to heat, atmospheric oxygen and water. Lubricants often contain two antioxidants that act in a synergistic manner. Antioxidants limit the oil degradation rate but over time become depleted.

Common antioxidants in hydraulic fluids are measured over the region 3700–3595 cm^{-1}. The left baseline, high wave number side, is taken as the minima in the region of 4000–3820 cm^{-1} and a right baseline, low wave number side, as the minima in the region of 2200–1800 cm^{-1}. For polyol ester fluids, antioxidants are measured over the region of 3400–3320 cm^{-1} using the same baseline correction.

Prediction of Oil Properties: Infrared analysis may also be used to predict some of the common oil properties usually determined from ASTM/DIN property tests. The desired physical property may be determined by mathematical procedures such as PCR (principal component regression) and/or PLS (partial least squares). PCR/PLS analysis routines interpret specific regions in the IR spectrum instead of individual peaks. The procedure requires a sample set covering the desired range of the property values in new and used oils in order to generate a calibration curve that can predict the unknown sample value of properties such as base number and viscosity [24]. The calibration matrix must cover all potential oil problems, contaminates, sources and mixtures. Whilst straight trend analyses of absorbance are relatively insensitive to minor oil changes, a calibration set that does not take into account the many differences in new and in-service oil chemistries will generate erroneous results. Calibration matrices must be maintained on a continuous basis to ensure continued reproducibility in results.

16.3.3 Electronic Particle Counting

Fine particulate contamination is the number one cause of failure for close tolerance hydraulic and lubrication systems. Electronic particle counting is the preferred method to determine and monitor fluid cleanliness.

There are a number of particle counters available in benchtop, portable and online versions. Figure 16.18 shows the sample path through a typical light extinction particle counter. These instruments utilize a collimated light beam that passes through the sample cell to a photodetector. The detector generates an electrical output that is proportional to particle size and count. When an opaque particle passes through the beam, it blocks an amount of light proportional to its size. The resultant change in the electrical signal at the detector is analysed against a calibration standard to generate particle size and count information. The instrument is equipped with a controller that divides (‘bins’) the various particles according to size. From this information, a direct reading of the cleanliness value is automatically determined.

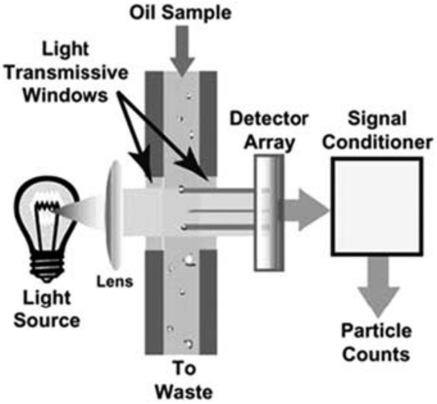


Fig. 16.18 Particle counter concept

Real-time particulate monitoring is accomplished by in-line flow-through sensors. Online particle sensors are miniaturized and packaged in a rugged casing to withstand the rigors of online machinery operation. State-of-the-art online particle sensors are integrated with, or contain, integral flow controllers. The flow controller is mandatory for particle count reproducibility.

Light extinction counters are adversely affected by fluid opacity, entrained air bubbles and water contamination. Fluid opacity degrades the signal levels of the instrument and a point can be reached where the instrument is no longer effective. Entrained air or water bubbles are counted as particles and thus give erroneous results. Fluid opacity can be partially overcome by diluting the oil with a clear solvent. In most cases, an inlet oil pressure of 5–6 bar will reduce air bubble interference to an acceptable level. Entrained air can also be removed during sample preparation by a combination of ultrasonic agitation and a vacuum. Particle counters do not remove water bubbles. However, high operating oil temperatures will reduce free water problems. For machinery systems that are prone to water contamination, the oil should be tested for water contamination before particle counting is performed. Note that any significant water level, >1000 ppm, will by itself, usually condemn the oil.

With supplementary filtering and clean oil makeup, the particle count can be expected to maintain a nominal value or ‘dynamic equilibrium’. This ‘baseline’ represents the normal condition of the system. Any increase in particulate counts above the baseline indicates an increase in contamination, regardless of whether the particles are wear metals, ingress dirt or oil degradation by-products.

Since the number of particles per millilitre increases dramatically as particle size diminishes, both the size and count data must be interpreted to determine the potential effect on a given machinery/fluid system. The interpretation is further complicated by the fact that even small changes in the count bin sizes will have a dramatic effect on counts recorded. To overcome this problem, the ISO community established the ISO 4406 and ISO 11171 standards for fluid cleanliness monitoring [25, 26]. The 4406 standard characterizes fluid cleanliness in increments from 0.01

to 2,500,000 particles per ml of sample and specifies three bin ranges and a series of numerical codes to indicate the count in each bin, where:

– the first code indicates the particle count above 4 μm,
– the second code indicates the particle count above 6 μm and
– the third code indicates the particle count above 14 μm.

The system is open ended and can expand in either direction, above or below the current codes. In practice, particle count data from a counter are compared to the ISO 4406 table for determination of the ISO cleanliness rating for each size range (Table 16.3). For example, a sample containing 80–160 particles/ml greater than 4 μm, 20–40 particles/ml greater than 6 μm and 5–10 particles/ml greater than 14 μm, would generate a cleanliness code of 14/12/10.

Table 16.3 ISO 4406 Table code numbers for maximum and minimum particle counts

ISO code	Min. count	Max. count	ISO code	Min. count	Max. count
1	0.01	0.02	15	160	320
2	0.02	0.04	16	320	640
3	0.04	0.08	17	640	1300
4	0.08	0.16	18	1300	2500
5	0.16	0.32	19	2500	5000
6	0.32	0.64	20	5000	10000
7	0.64	1.3	21	10000	20000
8	1.3	2.5	22	20000	40000
9	2.5	5	23	40000	80000
10	5	10	24	80000	160000
11	10	20	25	160000	320000
12	20	40	26	320000	640000
13	40	80	27	640000	1300000
14	80	160	28	1300000	2500000

ISO 11171 specifies calibration parameters for instruments and sensors. Repeatability and reproducibility of particle counters are ensured by a traceable standard such as provided by the National Institute of Standards and Technology (NIST). The medium test dust (MTD) reference fluid SRM-2806A is used to certify that particle counters correctly determine the count and size distribution of particles. The ISO 11171 standard specifies the maximum allowable percent differences in particle counts between test runs. Only counters that are certified as passing the ISO 11171 standard should be used for oil condition monitoring [27].

16.3.4 Elemental (Metals) Measurement

Many contaminants and oil constituents contain metallic elements that can be measured to determine relative concentration. The most effective and least costly method for measuring metallic content of lubricating oils is by elemental spectroscopy for which there are several variations.

Atomic Emission (AE) Spectroscopy: The most common wear metal measurement technique for general purpose oil analysis is AE spectroscopy [28]. AE determines the elemental constituents of wear metals by raising atomized elements to an excited energy state in a high temperature source. Characteristic emission lines are produced when one of the outer shell electrons is expelled from the excited atoms. The empty electron orbit can now be filled by a nearby electron that drops into the open orbit and emits its excess energy as a photon at a specific wavelength in, or near to, the visible light range. The wavelength of the photon (emission line) identifies the chemical element of the emitting atom. The emission energy produced by the excited atoms passes from the source through an entrance slit to a diffraction grating that separates the individual emission lines for each element. The intensity of each emission line is measured by a photomultiplier or digital array detector.

Standards define a calibration curve that is used to convert the element intensity values into parts per million (ppm) over a specific measurement range. AE may utilize multiple sets of calibration curves for different analysis applications. Simultaneous instruments measure all elements in a single cycle and can provide data on 20–60 elements in less than a minute. The two most common excitation sources for AE oil analysers are the rotary disk electrode type, commonly referred to as RDE, Rotrode or Arc/Spark and the inductively coupled plasma (ICP) type.

The Rotary Disk Electrode (RDE) – ASTM D6595: The RDE instrument has this name because the sample fluid is transported into a high temperature arc by means of a rotary carbon disc. The disc is immersed into the sample vessel, usually the bottle cover, and picks up oil and wear metals as it turns. The arc raises the energy states of the metal atoms in the oil causing them to emit their characteristic emission lines.

Some instruments have fixed burn times of about 30 s, whilst others have a variable burn time determined by measuring the hydrogen line emitted from the lubricant itself. The fixed burn time instrument may normalize its intensity results by measuring the hydrogen line. These technology implementation differences will cause analytical results to be significantly different for the same sample. The RDE spectrometer generally measures metal particles in the 0–10-μm diameter range. The emission line intensities for each element is integrated and converted to ppm by a preset calibration curve (matrix).

Whilst the measurement detection and repeatability limits of RDE instruments are in the low parts per million range, the results (for the same sample) provided by a particular manufacturer's instrument will depend on the arc source type and energy, the background correction method, burn time, sample viscosity and the metal particle size distribution in the sample. While individual instruments will generally produce reliable results for used oil analysis, those laboratories requiring multiple instruments should always choose a single manufacturer's type and model.

Inductively Coupled Plasma (ICP) – ASTM D5185: In the ICP method, argon gas is passed through a radio frequency induction coil and heated to a temperature of 8000–10,000 K, producing a plasma. The oil sample, diluted by a low viscosity solvent such as xylene or kerosene, is nebulized and borne by the argon gas carrier into the centre of the plasma torch. The high temperatures excite the metal atoms, which radiate their characteristic emission lines. The emission lines are captured and measured by the optical system.

The ICP method has superior accuracy, precision and repeatability over the RDE. ICP has a large linear dynamic range which permits single emission lines to measure a wide range of concentration levels. ICP can provide parts-per-billion (ppb) sensitivity. The spectrometer generally measures metal particles in the 0–3-μm range. Like the RDE instrument, the emission line intensities for each element are also integrated and converted to ppm by a preset calibration curve. Unlike the RDE, an ICP does not integrate large particles in the overall results. The measurable particle size distribution range is smaller than that of the RDE instrument, thus the absolute quantity of a given metal (ppm reading) measured is less. This measurement sensitivity drop-off is evident by the data shown in Table 16.4. However, lower ICP readings for the same sample do not adversely affect the instrument's reliability for condition monitoring. Statistical analysis of the readings for a target population of machines may be utilized to develop limits that commensurate with the instrument's measurement capability [2]. Lower general readings generate lower limits but the alarm timing is essentially the same.

Table 16.4 GE 16-7FDL diesel engine data from RDS and ICP spectrometers

	Pb	Cu	Sn	Fe	Cr	Al	B	Na
RDS Spectrometer								
Fleet average	15.4	9.0	0.6	22.6	3.0	4.0	4.5	38.3
Standard deviation	4.5	3.9	0.8	4.9	0.4	1.7	5.3	16.7
ICP Spectrometer								
Fleet average	1.2	4.0	0.2	10.0	0.3	2.3	1.6	18.4
Standard deviation	1.8	2.8	0.7	3.2	0.4	0.5	1.1	9.7

X-Ray Fluorescence (XRF) Spectroscopy: X-ray fluorescence may be understood by comparison to AE spectrometric methods. In an X-ray fluorescence spectrometer each atom radiates characteristic emission lines in the X-ray region when stimulated by specific energy. The XRF source generates high-energy photons (X-rays), which displace inner shell electrons in the target sample. Outer shell electrons then fill the vacancy left by the displaced electron. In doing so, they emit a characteristic X-ray photon (fluorescence) equivalent to the energy difference between the two states. Since each element has electrons with unique energy levels, the energy emitted in kV is characteristic of the element. And, the intensity of energy emitted is proportional to the elements' concentration (measured in counts per second). Thus a particular energy level measured at a specific count-per-second identifies an element and provides its relative concentration. Figure 16.19 shows the spectrum for a thin film containing several elements. The elements are identified by the energy level of the peak, e.g. 6.40 kV for iron (Fe). The amount of iron is determined from the intensity, in this case ~1950 counts per second (cps).

The XRF spectrometer utilizes an X-ray source to irradiate a small quantity of the sample. The X-ray source raises the energy level of the atoms in the sample, resulting in a corresponding release of X-ray energy by the excited atoms. Depending

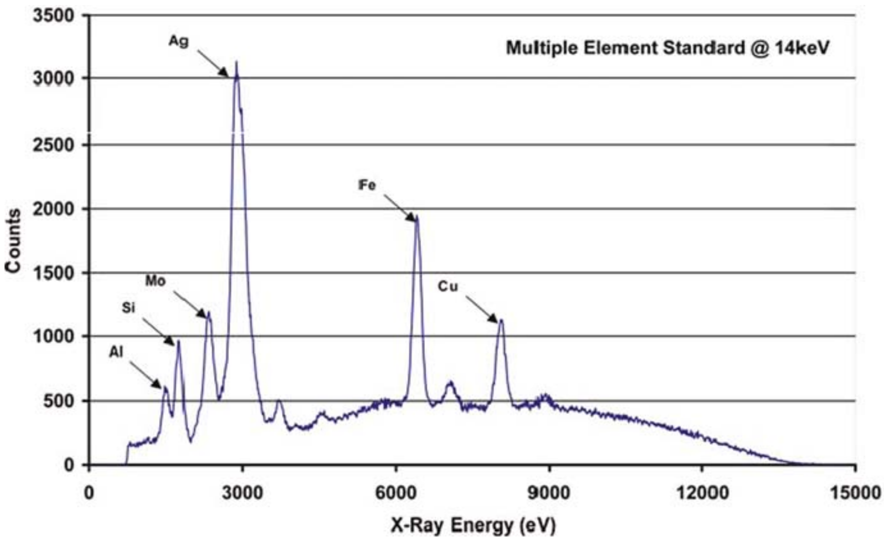


Fig. 16.19 XRF spectrum of a multi-element thin film

on the application, XRF can be produced by an electronic X-ray tube such as palladium (Pd) or silver (Ag), or a radioisotope source such as cadmium-109 (Cd) or americium-241 (Am). Recent advances in X-ray tube miniaturization have made it the preferred energy source for most benchtop and sensor spectrometer applications. The non-radioactive X-ray tube has the added advantage of safety and regulatory convenience. A detector captures the emitted X-ray photons. The detector signal is amplified and processed by a multi-channel data analyser. Spectral data may be displayed or reduced to elemental or corresponding metal alloy information.

XRF analysis technology has been widely developed for general purpose portable and benchtop metal analysers and specialized industrial and aerospace applications. In addition, XRF technology has also been applied to filter debris analysis [29], and to real-time lubricant analysis utilizing an in-line partial flow-through cell.

Online sensors provide an additional benefit in that the analysis time may be substantially increased thereby improving the reliable detection limits of the sensor. The bulk mass of the metal particles flowing past the sensor is integrated over several minutes or even hours to provide a reliable measurement of wear metals. From the average-integrated readings, a baseline can be established from which increasing wear rates can be determined.

16.3.5 Viscosity Analysis

Lubricant viscosity in and of itself is not a lubricant failure mode. However, any significant increase or decrease in viscosity is a symptom of a real oil failure mode.

For example, low viscosity may be attributed to molecular cracking (shear) or dilution by a lower viscosity fluid such as fuel. High viscosity may be attributed to oil oxidation or contamination by a more viscous fluid.

The most common viscosity test is the kinematic viscosity method (ASTM D445, IP-71, DIN 51566 and ISO 3104). Note that lubricant viscosity is discussed in detail in the next chapter. The kinematic viscosity is the product of the time of flow and the calibration factor of the instrument. The test determines the kinematic viscosity of liquid lubricants by measuring the time taken for a specific volume of the liquid to flow through a calibrated glass capillary viscometer under specified driving head (gravity) and temperature conditions. The test is usually performed at a lubricant temperature of 40°C and/or 100°C to standardize the results obtained and allow comparison among different users.

The test method is applicable to both transparent and opaque fluids. The unit of measurement for kinematic viscosity is the Stoke – equal to 1 cm^2 per second. For most lubricant applications, the Stoke is an inconveniently large unit and a smaller unit, the centistoke (cSt) – equal to 1 mm^2 per second – is preferred.

16.3.6 Supplemental Oil Tests

Used oil analysis is sometimes supplemented with additional test methods [28]. These tests are usually performed to meet a specific machinery monitoring requirement, to verify condition test alarms or to obtain data with a greater accuracy or reproducibility.

Gas Chromatography: Many condition monitoring laboratories utilize gas chromatography, GC, to verify the presence of specific molecular constituents or contaminants. The instrument uses a column to separate and measure chemical compounds by molecular weight, light first, heavy last. The instrument is particularly useful for detecting and measuring hydrocarbon components and contaminants of new and in-service machinery fluids. The most common application for GC in used oil analysis is to measure the concentration of fuel and antifreeze in used crankcase oils.

Diesel Fuel Measurement – ASTM D3524: The ASTM D3524 gas chromatography test determines the concentration of diesel fuel in motor oils.

Trace Glycol Measurement – ASTM D4291: The ASTM D4291 test determines the concentration of ethylene glycol in motor oils. The D4291 test is suitable for measuring trace levels of antifreeze (5–200 ppm). These techniques require standardizing with the specific fluids utilized by the machinery end user.

The 'Fuel Sniffer' Sensor: The Fuel Sniffer is a portable fuel dilution meter that can be used in the laboratory or in the field to provide rapid measurements of fuel contamination in engine oil. Developed in collaboration with the US navy, the Fuel Sniffer employs a surface acoustic wave (SAW) vapour microsensor to measure the concentration of distillate fuel in used diesel lubricating oil samples. The sensor quantifies the absorbed hydrocarbons by a change in frequency. The instrument samples the 'head space' in the sample bottle and calculates the percent of fuel present based on Henry's Law, which relates the fuel vapour concentration to the fuel present in the oil sample. The Sniffer has a measurement range of 2–10% fuel dilution for diesel, gasoline or other light distillate hydrocarbons. Its measurement accuracy is ±0.2% over the valid range if calibrated with the user's fuel and oil types.

Glycol Base Antifreeze Test – ASTM D2982: This method determines the presence of glycol-based antifreeze in petroleum engine oils. The glycol is extracted from the sample with an acid, oxidized and indicated calorimetrically as none, trace or positive. The test reagents are available in tablet and solution forms.

Karl Fischer Titration – ASTM D6304: The Karl Fischer titration, KFT, method determines water concentration by titrating a measured amount of sample and Karl Fischer reagent. The reagent reacts with the OH molecules present in the moisture, and present in other compounds, and depolarizes an electrode. The corresponding potentiometric change is used to determine the titration end point and calculates the concentration value for water. KFT reagents include iodine, methanol and chloroform and thus require a separate waste stream due to the chloroform.

KFT analysis is useful when oil additives interfere with infrared water detection methods, particularly true for oil with emulsifier or demulsifier additives as used in hydraulic and steam turbine oils. Conversely, some oil additives such as those found in diesel engine oil react with KFT reagents, yielding false results. In this case the infrared water analysis should be utilized.

Antioxidant Condition by RULER®, ASTM D6810 and D6971: The RULER® is a portable instrument for determining the 'remaining useful life' of machinery fluids based on their oxidative resistance levels. The instrument was developed to function with petroleum, synthetic hydrocarbon, ester-based and biodegradable lubricants.

Utilizing a voltammetric measurement technique, the RULER® quantitatively analyses the relative concentrations of antioxidants (hindered phenolic and aromatic amine) in new and used oils. This data can be trended to determine the depletion rates of the antioxidant protection package in the oil provided the instrument has been calibrated for that oil type. From pre-established limits, proper oil change cycles, potential interval extension or timely antioxidant replenishments can be determined.

16.4 Condition Data Management

16.4.1 Introduction to Managing Condition Data

Regardless of the test methods utilized, the oil analyst may observe condition data that are being simultaneously generated by more than one fault mechanism source where both fluid contamination and degradation parameters may change. Very seldom does a failure mode result in only a single fault mechanism, although often a single root cause can be found. Consequently, subjective or qualitative data do not provide reliable indicators of failure mode presence and progress. Reliable data interpretation of fault initiation and its progress towards failure requires *numerical* condition data.

Numerical data provide an effective trending capability and in conjunction with statistical analysis ensure reliable fault detection and severity assessment. Note that fluid samples must be collected frequently in order to provide reliable ‘early detection’ and trend granularity. In-line sensors employing real-time data collection will overcome this problem. In addition, test data must be of the highest quality. Poor sample collection practice, poor analytical practice, improper data storage or insufficient data integrity checks generate data that cannot be interpreted properly or provide reliable statistics.

16.4.2 Maintenance and Storage of Data

Maintenance and monitoring systems generate vast quantities of data that must be validated and stored by electronic means to facilitate economical analysis and report generation. In addition, the data storage technology must be kept current in terms of hardware and software and be accessible by the latest automated analysis tools or a complete data analysis may be impractical to perform. Thus, any effective condition monitoring plan must provide a complete description of the data management system including:

- each data item, its relevance and relationships,
- the procedures in which the data items are used,
- the principles and algorithms used to reduce and evaluate each data item including how to identify out-of-context, corrupt or bogus data,
- the applicable equipment fault and symptom libraries,
- all hardware and software, including functions libraries, expert systems, instrument interfaces, communication protocols and standards and
- the procedures to be used to verify and maintain the data system after implementation.

It is preferable that the monitoring and machinery databases are integrated. If the databases are not integrated, data must be entered separately into each, increasing the probability of error. Moreover, non-integrated or non-relational databases cannot be easily used for condition or reliability assessment.

16.4.3 Data Interpretation

The authors have been involved in the development and deployment of advanced oil analysis systems including completely automated expert systems for data interpretation and maintenance action recommendation. The data analysis principles utilized in these systems are not new. The Canadian Pacific Railway first utilized expert systems for oil data interpretation in 1985 [30]. Subsequently, the paradigm utilized in the CPR system was confirmed by expert system development projects in numerous naval, railways, mining and commercial laboratories [31].

The principles utilized in these expert systems are general purpose and based on failure modes, effects and critically analysis, FMECA, a sub-process of reliability centred maintenance, RCM, and statistical process control, SPC. The analysis paradigm includes:

- procedures for trending parametric data according to sampling and maintenance conditions. Parameter trends are calculated using an adaptive procedure [2]. The trend subsystem gives the best available trend value for each test parameter depending on operating circumstances as sequenced by rules in the expert system. Trend data granularity is ensured by an optimum sample interval as determined from FMECA on the target equipment fleet. The sample interval must be shorter than the interval from fault initiation to failure for the shortest critical failure mode.
- a raw data reduction procedure to reduce all condition data to relevant statuses for both level, or concentration, and trend, as the rate of change, measurements. Statistically based limits are used to generate the status data.
- a procedure to distinguish between individual machines in a fleet. Used oil data from individual machines in a fleet can be expected to range above and below the mean fleet 'normal' value. Minimum and maximum values can range considerably depending on operating conditions. The expert system interpretation procedure considers the statistical rank of the lubrication system within the population of like systems. The status of parametric condition indicators may be increased or decreased depending on whether the raw data are a high reader or low reader.
- a procedure to determine condition indicator data from parametric measurements.
- a procedure to determine and confirm the presence of one or more failure modes based on fault signature analysis.

16.4.4 Data Interpretation Procedure

Lubricant condition monitoring is best accomplished by the analysis of numerical data that are associated with the various fluid failure modes [2]. Numerical data can be analysed by statistical methods to determine the relationship between the various test parameters and their respective fluid and machinery failure modes. In addition, the statistical analysis can be used to determine potential data interference sources, the various alarm limits for each parameter and other criteria to be used in the daily evaluation of used oil. Note that it is important to determine 'all of the causes' for variability in parametric data, just as it is necessary to separate changes due to interfering causes from changes with its associated relevant failure modes.

Oil data interpretation can be divided into four simple steps, each with its associated databases and evaluation criteria (Fig. 16.20). These procedures are reliable when data variability due to events other than failure modes is under control.

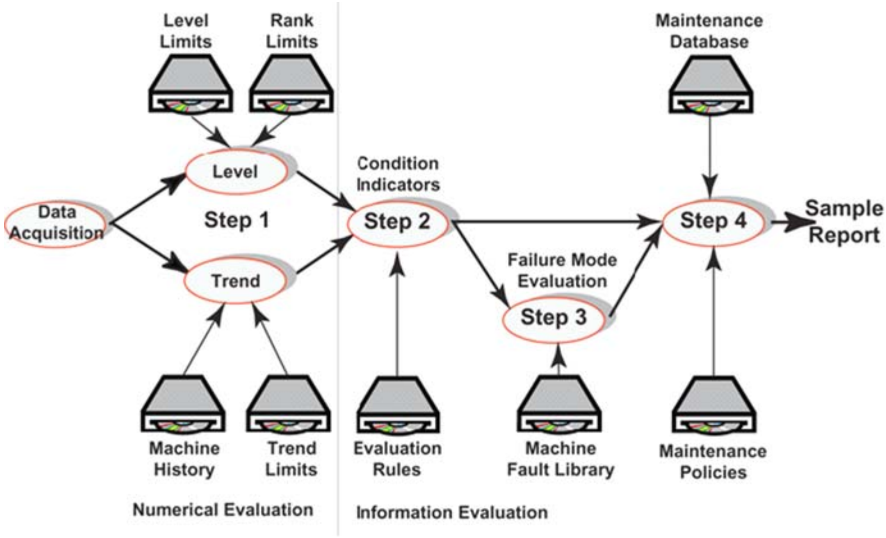


Fig. 16.20 Data interpretation procedure

Step #1 reduces infinitely variable analogue numbers to distinct incremental status values that are more readily understood and interpreted. This process uses current sample, historical and statistical data to completely define the meaning of each oil test parameter in simple common language terms. For example:

- Level status: *normal, marginal or reportable*
- Trend status: *decreasing, stable, moderately increasing, rapidly increasing*
- Rank status: *high reader, nominal or low reader*.

For simplicity, all oil test parameters are defined by the same attributes and each attribute's status is established by appropriate statistically based limits. It is important to remember that parameter level is a scalar of how much damage has occurred, such as contaminant concentration. Parameter trend is a scalar of how fast the damage is occurring and thus a measure of the remaining time to failure. Reliable interpretation of the machine/fluid condition requires an analysis of both parameter level and trend amongst other relevant data, such as statistical rank, that are an indication of individual machine dynamic equilibrium with respect to the fleet mean readings.

Step #2 combines test data attribute statuses to generate a uniform *Condition Indicator* status for each oil test parameter. For example:

- Condition indicator status: *normal, alert, urgent, hazard or danger*.

The meaning of the condition indicator status is related to the appropriate maintenance response as required by corporate policy. For example:

- Normal: maintenance not required, continue routine sampling
- Alert: monitor closely, shorten sample interval if necessary
- Urgent: maintenance is recommended, deferral is permitted

– Hazard: maintenance is required, no deferral permitted
– Danger: shut machine down, do not operate until maintenance is completed.

Table 16.5 shows a generic interpretation for kinematic viscosity data for large diesel engines. The matrix indicates the viscosity condition indicator status and potential cause for the various viscosity level and trend statuses.

Table 16.5 Example – viscosity condition indicator/failure mode matrix

Level status	Trend status	Condition indicator	Potential cause
Low nominal	Decreasing	Alert	Increasing fuel dilution
Nominal	Stable	Normal	Nominal operation
Nominal	Increasing	Normal	Nominal operation
Low marginal	Decreasing	Urgent	Increasing fuel dilution
Marginal	Stable	Stable	Stable operation
High marginal	Increasing	Increasing	Increasing oil oxidation
Low reportable	Decreasing	Danger	Increasing fuel dilution
Low reportable	Stable	Hazard	High fuel dilution
High reportable	Increasing	Urgent	Increasing oil oxidation

The evaluation matrix consistently generates the same level of alarm for the same probable risk regardless of whether the abnormal condition is driven by high trends or condemning limits.

A condition indicator can sometimes indicate an abnormal state for other reasons such as false positives, bad samples, multiple occurring fault signatures, improper maintenance, unreported maintenance or the lack of maintenance. Other evaluation steps are necessary to ensure an accurate recommendation response and eliminate any potential false positive.

Step #3 compares all abnormal condition indicator statuses to a library of fault signatures to arrive at a diagnosis. A positive diagnosis increases the certainty that an abnormal data indication is justifiably abnormal and rates a maintenance response. The fault signature library contains signatures for all known faults, bad sample indications, false positive indications, inappropriate trend indications or any known symptom that could impact the accuracy or reliability of an intended maintenance response. Table 16.6 shows the potential interpretations for kinematic viscosity changes from normal in a diesel engine application. The interpretation combines

Table 16.6 Example diesel engine oil failure mode fault signatures

Fault	Indicators
Fuel dilution	Low viscosity and high IR fuel
Oil oxidation	High viscosity and (high IR Oxid, high IR Nitr, high IR Sulf, low BN)
Wrong oil addition	Wrong viscosity and (low Ca, wrong IR foreign oil)
Molecular shear	Low viscosity and no IR fuel
False positive	Low viscosity and high IR water

viscosity and infrared analysis data to resolve the various failure modes that cause a change in viscosity.

Step #4 combines diagnosis and condition indicator status levels and generates an overall risk of failure indication. Typically the worst case condition indicator severity is used to indicate the fluid condition status. Since the diagnosis will relate to a specific maintenance or inspection instruction, this procedure requires a search of the user's maintenance database for previous and scheduled work. Once the maintenance data are known, the fault diagnosis reports the appropriate maintenance response from the users' troubleshooting instructions.

16.4.5 Condition Indicators

Level and trend status data are fused to improve problem risk determination reliability, properly gauge the extent of damage that has occurred and how rapidly the damage is occurring. History shows that oil analyses sample populations contain examples of parametric data that have exceeded magnitude limits by other than failure-related data excursions. For example, a parameter such as a wear metal may slowly increase and exceed a level limit due to a closed lubrication system where oil consumption is low. This is an indication of increasing concentration but unless the contaminant itself is harmful to the machinery/fluid system, it may not be a reason for alarm. In addition, slowly decreasing oil quantities will also signal increasing parameter levels, again without indicating a severe condition is present. Parameter levels rise due to accumulation and fall due to makeup oil dilution. Proper interpretation will require consideration of these factors.

Condition indicator severity values are generally reliable, however, there are conditions such as bogus samples, incorrect labelling, wrong sample order, improper maintenance that can satisfy the numeric test limits and erroneously indicate the presence of a failure mode. Oil analysis expert systems should contain additional rules to eliminate false positive diagnostics wherein positive condition indicator exceedence(s) are compared to specific fault mode signatures. The possibility of an erroneous alarm condition coupled with a positive failure mode diagnosis is remote. This diagnostic step greatly improves the probability that abnormal data readings are the result of a real alarm condition. Finally, diagnostic data, maintenance data, and maintenance instructions are evaluated to generate an appropriate recommendation. The analysis is consistent, reliable and thorough.

The second essential component to the statistically based data interpretation philosophy centres on the maintenance of the expert system knowledge base. Oil analysis expert systems, like any human engineering endeavour, are bound to have complex features and require some means for effective analysis and update. In the case of oil analysis expert systems, equipment operation and maintenance have a major impact on data variability and thus a major impact on data analysis complexity and reliability.

The key to obtaining reliable oil data is controlling those factors that cause data variability, or at least, recognizing those factors, and utilizing compensating rules in the expert system knowledge base. Statistical analysis of equipment usage, remaining component life, repair history, oil addition history and other maintenance events provide considerable insight into how oil data are affected by operations and maintenance. While the expert system data interpretation paradigm is based on RCM concepts, SPC provides the genesis for system validation and maintenance. In an RCM/SPC approach, the operation of an equipment fleet is viewed as a closed loop (Fig. 16.21). Operations and maintenance provide the system stimulus. Oil and usage monitoring provide the control feedback. As equipment operators and maintainers influence the system, oil and usage measurements are also influenced. Under the closed loop paradigm, the equipment utilization causes changes in test data, maintenance actions counteract these changes (e.g. new oil additions), thus the test data attain a dynamic equilibrium state, where deviations in oil measurements – failure signatures – stand out and can be interpreted by standard data interpretation procedures. Changes in oil data not attributed to an operation or maintenance event are usually an indication of the presence of an abnormal or failure mode.

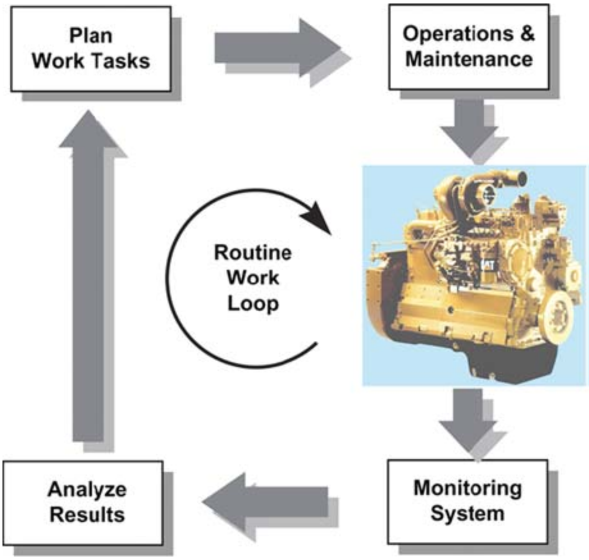


Fig. 16.21 The RCM work process

In this environment, limits can be easily established by a statistical analysis of historical data from each population of machines. During the implementation of expert systems, all limits for fluid condition are verified by statistical analysis of test data. Limits are calculated from the following formulae [2]:

$$\begin{aligned}\text{Marginal Limit} &= \text{Average} + \text{Two Standard Deviations}\\ \text{Reportable Limit} &= \text{Average} + \text{Four Standard Deviations}\\ \text{Moderate Increase Limit} &= 60\% \text{ of Marginal Limit}\\ \text{Rapid Increase Limit} &= 90\% \text{ of Marginal Limit}\end{aligned}$$

Figure 16.22 shows the frequency distribution of kinematic viscosity measurements of a population of 32,000 samples from a locomotive diesel engine fleet. This population includes data from all faults as well as false positives indicated by values less than 6 centistokes (cSt). The false positives result from kinematic viscometer failure when significant water is present. The mean and standard deviation for the raw population are 15.2 cSt and 1.4 cSt, respectively. For proper statistical limits to be calculated, the false positives and extremely high readings due to failed oil must be removed. Over-representation of a failure mode in the sample population will generate a limit that is too high, while under-representation will generate a limit that is too low. Generally, culling sample values four Sigma above and below the mean will accomplish the goal of removing extreme data values that skew the limits calculation.

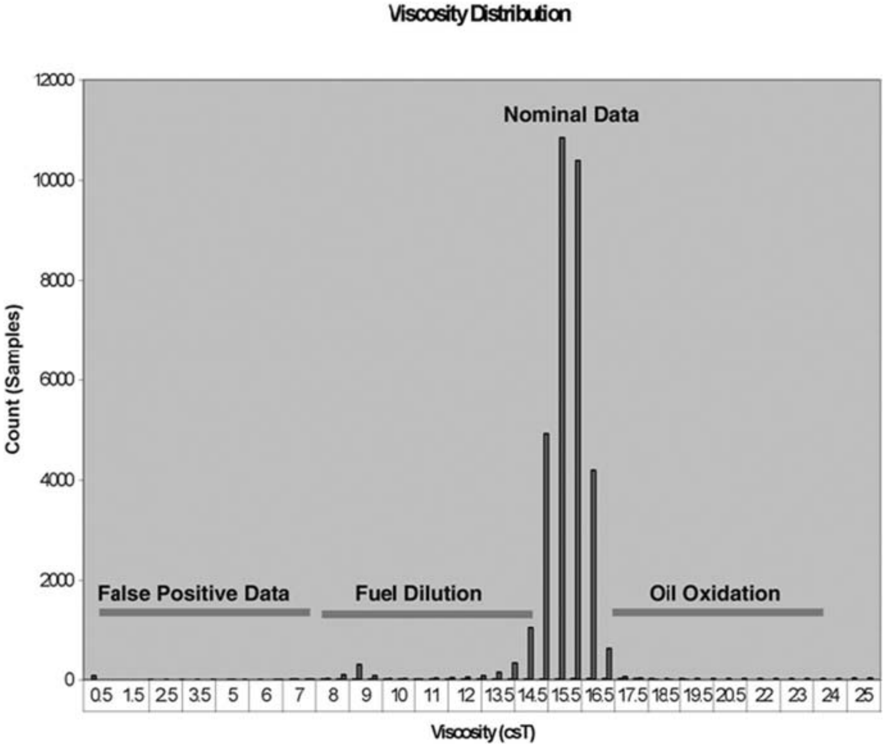


Fig. 16.22 Viscosity data frequency distribution

Table 16.7 is an example of viscosity limits for a medium speed diesel engine selected from the culled sample population in Fig. 16.22. These limits will reliably indicate fuel dilution and oil oxidation problems for the specific lubricant and fuel used.

Table 16.7 Example of diesel engine oil alarm limits for viscosity

Viscosity mean	Viscosity standard deviation	Low reportable	Low marginal	High marginal	High reportable
14.4	0.7	12.6	14.0	17.2	18.2

The limits are implemented and subsequently refined by additional calculations on an ever-increasing sample population and by experience from systems and reliability analysts. Note that statistically based limits are maintained only if realistic sampling and maintenance practices prevail. In addition, the limits are dependent on the normal proportion of failure modes and normal data in the database.

16.5 Conclusion

In conclusion, oil data interpretation is mathematically feasible for equipment fleets where there is sufficient history of all critical failure modes and respective maintenance responses. Most operators of large equipment fleets or equipment that has been in use for long periods of time have sufficient historical data to determine data interpretation criteria and the impact of operations on oil data reliability and to map the specific events that affect data integrity. Lubricant analysis expert systems are in daily operation confirming the stability and reliability of the procedures used.

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Chapter 17
Automotive Lubricant Specification and Testing

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Abstract This chapter concerns commercial lubricant specification and testing, drawing together the many themes of previous chapters. Military lubricant standards were a very strong initial influence during World War II and led to the separate historical development of the North American and European specification systems. The wide range of functions that a successful lubricant must satisfy is discussed, together with issues of balancing special or universal applications, single or multiple engine tests, the philosophy of accelerated testing and the question of 'who sets the standards?' The role of engine tests and testing organisations is examined.

Development of the tripartite API/SAE/ASTM specification system is described through to the current (2008) SM (petrol/gasoline) and CJ-4 (diesel) specifications, set out as tables. The roles of the US lubricant and vehicle manufacturers in forming these specifications are discussed. External and internal drivers for current and future changes are described and assessed, such as increased service intervals, higher performance levels and environmental changes leading to higher soot levels. The separate development of the European specification system through the CEC system and the different relationships between lubricants and OEM manufacturers, relative to North America, are described. The reasons for the evolution of the CEC system into the ACEA system are described and the current specifications set out as a table. The role of associate organisations such as ATIEL is explained. The evolution of the GF-series under the ILSAC specification system is described. Examples are given of specific engine and laboratory tests. The direction of future engine lubrication specifications and the forces shaping them are examined.

17.1 Introduction

17.1.1 Prior to 1940

This chapter is appropriately concerned with the specification and testing of automotive lubricant products. It draws together the many strands of previous chapters

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in describing lubricant specifications for service use to ensure that those specifications are met. Since World War II, development has been driven by the automotive industries, initially North America and Western Europe and now increasingly global. But lubricant specifications and supporting tests have developed differently across continents and convergence towards a unified system has been slight, if at all. Various ‘players’ in lubricant development have had varying influence over the years, between lubricant suppliers, additive industry, original equipment manufacturers (OEMs) and end users. The crucial point is that OEMs have final responsibility for their product’s performance warranties in an increasingly consumer-focused market.

The three major lubricant classification and specification systems are the US API tripartite, European CEC-ACEA and the international ILSAC systems. The form of their lubricant test procedures shows why they have developed in their present separate forms and how they might converge in the future. For up to the mid-1930s there were no engine lubricant tests, lubricants were chosen on the basis that they ‘worked’, however defined, and where self-selection rejected ‘poor’ quality lubricants by essentially subjective tests for relatively lightly stressed engines. This rather unchallenged situation was upset in the mid-1930s by Caterpillar introducing new engines for their heavy duty tractor/heavy construction equipment which, for their time, were relatively high powered. Typically arduous operation using contemporary lubricants caused heavy, adherent, piston carbon deposits which rapidly ‘stuck’ piston rings such that engine efficiency rapidly declined. The advantages given by these characteristically rugged engines were negated by the need to dismantle, clean and re-assemble them after short periods of use. Recurrence of the same problems caused increased ‘down time’ – engine design technology had moved significantly ahead of contemporary lubricant technology.

Caterpillar showed that small amounts of ‘metal soap’ added to the lubricant countered the deleterious ‘carbonisation effect’ on engine performance, the first ‘detergent’ additive, aluminium dinaphthenate, thus introducing ‘additive chemistry’. Field test screening of newly developed but different lubricants gave variable long-term results and Caterpillar developed a laboratory engine test in 1940, designated ‘L-1’, to rapidly screen lubricants for field use. The US military soon required a rapid screening process for a diesel lubricant specification for ‘severe’ diesel engines such as Caterpillar’s.

Lubricants are an essential system component to be developed in parallel with engine technologies. Monograde lubricants dominated the 1950s, needing to be changed between ‘winter’ and ‘summer’ grades, whereas multigrade lubricants dominated the 1960s, initially the 20W50 grades, later the 15W40 grades, more recently a 0W20 grade for heavy duty diesel service, [3]. Improved base oil technology has low evaporative loss and improved cold flow properties by using Gp II/III highly refined base oils, Gp IV poly-alpha-olefins (PAOs) and Gp V synthetic esters, and others, to improve base oil performance. Biodegradable base oils are increasingly used in environmentally sensitive markets.

17.1.2 The Influence of Military Lubricant Standards

World War II accelerated lubricant development, driven by military engines and equipment operating at ever higher operational levels, an additional difficulty being the provision of meaningful/adequate servicing standards. The US Army MIL-2-104 standard was the minimum performance standard for heavy duty detergent lubricants in 1941, upgraded to MIL-2-104B in 1943. The US navy set their 14-013 lubricant specification in 1943 for the diesel engines in its submarine fleet. Overall, the US Department of Defence, then NATO, became the leading consumer specifiers of lubricant performance at that time.

US lubricant tests used large engines, whilst the UK developed similar, parallel tests using smaller local engines. Initially UK/Europe expected similar results to the larger US engines but the effects of smaller engines, different design philosophies and higher power densities were not appreciated at the time and gave different results. These two approaches led to the different current systems of engine lubricant tests.

The US military and UK MoD set lubricant specifications as users of mechanical equipment systems, rather than the manufacturers and independent of lubricant producers. US military committees, military personnel and representatives of equipment suppliers, developed specification and approval systems for lubricants used by US and worldwide lubricant manufacturers, other than ‘Eastern Bloc’ countries.

The European emphasis was different, where UK and other military authorities worked with the lubricant industry to develop their own tests and quality procedures. Larger US engines test-quality components were very expensive; it was cost-effective for European engine lubricant tests to develop locally sourced, smaller engines. The importance of military lubricant standards diminished in the 1980s and the influence of engine manufacturing groups grew. The US/European differences in test engines size and testing philosophies proliferated engine tests.

Whatever the specification system, successful engine lubricants must satisfy a wide range of functions. They must ensure the operating reliability of the many friction points in engines, Table 17.1, but additionally must seal and cool the piston/cylinder interface and also transport metallic debris, soot and degradation products to the filter. Hydrodynamic and elastohydrodynamic conditions exist in bearings, whilst boundary conditions exist at the top and bottom dead centres (TDC and BDC) of sliding piston simple harmonic motion. Temperatures can vary from –50°C at start-up to 100°C+ sump temperatures and >300°C peak values under the piston crown. The issues to be addressed for each lubricant formulation are included in Table 17.1.

17.1.3 Special Lubricant Requirements or Universal Application?

An initial problem with lubricant development was that engine manufacturers regarded their individual products as unique by metallurgy, design and use. Individual manufacturers wanted special lubricant tests in addition to general lubricant

Table 17.1 Issues for lubricant formulations in a four-stroke engine

Functions	Location	Oil properties	Test examples
Friction reduction	Bearings, pistons, rings and cylinders. Especially at cold start.	Low enough viscosity for when engine is cranking. Minimum viscosity under all ambient and engine conditions. Sufficient high-temperature viscosity, especially during mixed lubrication phases such as at TDC. Fuel economy.	M111FE Sequence VI-B OM602A/OM646LA
Wear protection	In normal running, at extremes of temperature and during shutdown.	Protect against corrosive wear effects of fuel decomposition products. Resist oxidative degradation and deposit formation. Reduce consequences of unavoidable metal–metal contact.	Sequence IVA Sequence VE TU3M, OM602A/OM646LA Sequence IIIG TU5, Ball rust test
Sealing	Between rings and cylinders	Sufficient viscosity at high temperatures, especially in the piston ring zone. Low volatility. Low deposit forming tendency in the ring grooves. Limit ring/liner wear	VW IC TD VW TDI Noack
Cooling	Mainly pistons, rings and con-rod bearings	Good thermal stability and oxidation resistance and low volatility.	Sequence IIIG, TU5 and Noack
Disperse contaminants	During the oil drain. Soot, fuel, sludge, soot, wear debris, dust, water.	Solubilise certain organic compounds (fuel and decomposition products and oil oxidation products). Be able to disperse a fine suspension of contaminants under all temperature, physical and chemical conditions.	DV4 M111 SL Sequence VE/VG

tests, thereby proliferating test standard requirements, increasing costs for each test and approval procedure. Formulating general lubricants for mixed vehicle fleets with different OEM engines was difficult.

The ILSAC system, developed by US and Japanese OEMs, has started to progressively rationalise lubricant tests on an international basis leading to the GF-(x) series of petrol engine standards but has not progressed as far as initially hoped.

Lubricant development does not progress within a constant frame of reference because base oil and additive qualities to formulate a final lubricant product are both increasing, e.g. Gp.I base oils are being replaced by Gp.II or III hydrocarbons or synthetic base oils, with additive pack action now much better understood and more robust. Resolution of conflicting properties and requirements of advanced lubricant formulations has been considerably improved. Environmental emission controls increasingly impinge on the performance requirements of lubricants, consumer interests increasingly expect longer intervals between service lubricant changes, for the same formulations.

17.1.4 Single Tests, Many Engines or Many Tests, Single Engine?

Early engine test developments were oriented towards one lubricant test property per type of engine test, e.g. piston cleanliness for lubricant detergency, sludge formation for lubricant dispersancy, engine component wear and component corrosion. This approach led to single tests on many engines, expensive and possibly confusing.

The current situation requires a wide range of tests for most specifications but OEMs want these tests for a specification to be conducted on one engine, reducing testing costs but raising difficulties if different engines have incompatible requirements. New engine lubricant test development is expensive, for the test itself, extensive committee works, tests hardware equipment and installs new equipment in many engine lubricant test houses across the world – considerably expensive and time consuming. These constraints tend to keep existing test procedures with minor incremental changes to engine test conditions or fuel formulations, but on the other hand, as engine testing is a mature technology then major and dramatic developments are not to be expected.

The realistic alternatives might be either simple laboratory chemical/physical tests which give quick results, but are too simplistic and do not reflect field experience, or real-life/on-road, service conditions over a very extended time period. It may be several years for results to be determined. If lubricant problems become obvious after a time then there are related product liability issues. These alternatives are usually unrealistic because of their overwhelming disadvantages. Accelerated mechanical engine lubricant testing may have disadvantages but, in general, is preferable to the alternatives.

17.1.5 'Accelerated Testing'

Engine lubricant tests use 'accelerated' conditions which means, inter alia, 'higher engine temperatures' as being higher and longer than normally experienced in service. The Arrhenius Activation Energy principle increases chemical reaction rates by a geometric factor of 2–3 for each incremental 10C° increase, 4–9 for a 20C° increase and 8–27 for a 30C° increase, etc. Higher power outputs, relating to the higher temperatures described, but also higher bearing loads, shear rates, increased valve spring loads, cam and tappet loadings and more severe fuel compositions, all of which produce the anticipated degradation effects in a much shorter time. An example is the M 111 sludge test which reduces the time taken for an engine test to begin showing deposits and wear.

Relationships between initial deposits or wear in an engine lubricant test and engine failure in service are not strong. Early 'deterioration', evidenced by the onset of wear/deposits, relates to test 'failure' by reference to scales of wear or deposits. The 'failure' parameter level set is not that would cause problems in service life but indicative. This testing philosophy limits the engine test length, and thus costs, preventing very expensive, potentially dangerous, catastrophic engine failure. Apart from the expense and danger, it is problematic to assess wear and deposits from the shattered components of a catastrophic engine failure. How meaningful the relationship is between engine test cell results and service life performance is strongly debated but a better, more consistently related, set of procedures has neither been developed nor found. Essentially, the API/ACEA classification and specification systems are proven to work for the overwhelming majority of automotive applications. However, the success of these systems should not close minds to the occasional exceptional cases of engine lubricant problems which arise from an unexpected combination of application and use.

17.1.6 Who Sets the Standards?

Should a manufacturer's new engine design accept an already available standard brand of lubricant, which may limit its long-term performance level? Or should the new design maintain its best mechanical performance, beyond the long-term lubrication performance of new engine available lubricants and requiring development of a new, higher quality lubricant for reliable performance?

Two views flow from these points – lubricant companies may see this as engine manufacturers using them to solve equipment problems. Alternatively, engine manufacturers regard the development of higher performance standard lubricants as part of system technological development, engine and lubricant considered together, to give advanced engine products. New vehicle aerodynamic design reduces available engine space, lubricant capacity and cooling air effects. The US and European situations have changed over the last four decades, where initially manufacturers designed engines to operate with the available good quality lubricants. But sharp changes in emission control requirements, extended service intervals, reduced engine capacities, higher power densities and fuel efficiency improvements have all severely increased the requirements for lubricant performance. Field problems together with enhanced lubricant requirements led US engine manufacturers to work with lubricant and additive manufacturers.

The predominant Japanese approach developed engines which satisfactorily operate with a range of lubricants, the ‘robust’ approach, particularly suited for manufacturing industry strongly oriented to exporting products to all countries and the varying standards of service regimes to be found there. However, within Japan the single automotive companies set stiff requirements for approval of preferred lubricants known as ‘Genuine’ lubricants.

Europe had wider approaches to lubricant approval from different countries, thus German OEMs set very comprehensive specifications with stringent targets. As field problems arise, specifications are amended. Whereas France had an approval regime where a single lubricant supplier worked closely with, and strongly supported, an engine OEM.

17.1.7 A Summary of Attitudes and Philosophies

Different engine lubricant testing approvals arise from different attitudes and philosophies in different continents and also different countries within those continents. Issues are now addressed internationally by new test method development and procedures for specifying lubricant qualities, leading to new approval systems. These developments benefit engine and equipment manufacturers, producers of lubricants and additives and, ultimately, users of mechanical systems of whatever form in an eventually international marketplace.

17.1.8 Testing Organisations, Their Roles and Engine Tests

Various organisations are involved in lubricant testing and specification procedures. Understanding the complexity of lubricant classifications is difficult, with organisation acronyms which may seem, superficially, to either overlap or duplicate each other. Relationships between organisations are complex and discussed in the next section for the three main regions of influence, API and the tripartite system for United States/North America, ACEA for Europe (now including the rapidly developing Eastern Europe market) and JASO of Japan, including Asia and the Pacific Rim countries. It is useful to understand these organisations’ development; their current positions and interactions can then be understood and their future development, possibly their convergence, reasonably predicted.

‘Realistic’ engine tests are only meaningful over field trials lasting 1 year, or more. But what is realistic? – the variety of engine use is almost as varied as life itself. To address this, international committees have defined engine lubricant tests which are practical, relevant to use and reproducible under tightly defined conditions.

Testing procedures, approval, standardisation and performance limits for lubricants in the United States are decided by the automotive industry and the API, given in Section 17.2. In Europe this responsibility is shared between CEC, which sets testing procedures, approvals and standardisations, with performance limits set by ACEA, decided with the additive and lubricant industries, given in Section 17.3. ILSAC has generally adopted the US automobile specifications for lower viscosity formulations, given in Section 17.4, with additional test requirements, in particular fuel efficiency tests.

17.1.9 General Principles

The general principles of engine lubricant testing address issues of:

- oxidative and thermal stability,
- the control, via dispersion and detergency of soot, varnishes/gum, degradation products and sludge formation,
- anti-bore wear and anti-corrosion protection,
- shear stability and anti-foaming tendency and
- fuel economy and fuel economy retention.

17.1.10 Specific Light Vehicle Engine Test Objectives

To meet these aims for light vehicle lubricant formulations, each engine test has a characteristic criterion or set of criteria, some examples are given in Table 17.2. These light engine lubricant tests are used for either or both petrol- and diesel-fuelled light vehicles as components of API or ACEA test procedures.

17.1.11 Specific Heavy Duty (Diesel) Vehicle Engine Tests

A selection of tests for heavy duty diesel engines showing the characteristic objective, or set of objectives, for each test, is specified in Table 17.3. The detailed procedure specification for each test is given on their individual web sites and in the appropriate tables for API, given in Section 17.2, ACEA, in Section 17.3 and ILSAC in Section 17.4, where appropriate.

17.1.12 The API, ACEA and ILSAC Lubricant Specification Systems

Sections 17.2, 17.3 and 17.4 look at the API tripartite, the ACEA and ILSAC lubricant specifications, respectively. The complete specification tables are not given for each system because:

Table 17.2 Engine lubricant tests for light vehicles, petrol/diesel

Test engine	Test procedure	Test assessment objectives
TU5JP-L4	CEC L-088-T-02	High-temperature deposits, ring sticking, Oil thickening and consumption
TU3M	CEC L-038-A-94	Valvetrain and scuffing wear
MIII SL	CEC L-053-T-95	Black sludge
MIII FE	CEC L-054-T-96	Fuel economy
VW 1.6 TCD	CEC L-046-T-93	Piston cleanliness and ring sticking
DV4 TD	CEC L-093	Medium temperature dispersivity
OM602A	CEC L-051-A-98	Wear, viscosity stability and oil consumption
OM646LA	CEC L-099-08	Cam and tappet wear, bore wear and polish, cleanliness and sludge formation
VW TDI	CEC-L-078-T-99	DI diesel piston cleanliness and ring sticking
SequenceVE	ASTM D5302	Low-temperature sludge and cam wear
Sequence VG	ASTM D6593	Low-temperature sludge
Sequence IIIF	ASTM D1491	Oxidation, wear, cleanliness
Sequence IIIG	ASTM D7320	Oxidation, wear, cleanliness
Sequence IIIGA	ASTM D4684	Aged oil low-temperature viscosity
Sequence IVA	ASTM D6891	Cam wear
Sequence VIII	ASTM D6709	Bearing corrosion
Sequence VIB	ASTM D6837	Fuel economy retention

Table 17.3 Some specific heavy duty (diesel) vehicle engine test objectives

Test engine	Test procedure	Test assessment objectives
Caterpillar 1 K/N/P		Piston cleanliness, wear, consumption
Cummins M11		Valvetrain wear, sludge
GM 6.21		Valvetrain wear
OM 364LA	CEC L-42-T-99	Piston cleanliness, cylinder wear and polish, sludge, lubricant consumption
OM 602A	CEC L-51-A-98	Wear, cleanliness, oxidation, lubricant consumption
OM646LA (Replaced OM602 in ACEA 2008	CEC L-099-08	Cam and tappet wear, bore wear and polish, piston cleanliness and sludge formation, using BO5 fuel
OM 441LA, replaced by OM501LA in ACEA 2008	CEC L-52-T-97	Piston cleanliness, cylinder wear, turbocharger deposits
OM501LA	CEC L-101-08	Bore polish, piston cleanliness, consumption, sludge, using BO5 fuel
Mack T-8E/11		Soot handling
VW TDI	CEC L-078-99	Piston cleanliness, ring sticking, TBN and TAN
Mack T-12		Wear of liner, ring and bearings

- the specification tables are very detailed and comprise a large set of pages with many footnotes and it is not the purpose of this chapter to exhaustively reproduce them,
- current and previous specification tables are available on their respective 'parent web sites' or on various company web sites, such as Infineum, http//.www.infineum.com,
- the specification tables are periodically reviewed, ACEA recently every 2 years, the next API revision, to API S(N?) and API C(K?), may occur within the next 2 years and ILSAC expects to revise GF-4 into GF-5 in the next 2 years and
- any lubrication specification tables given in this chapter will be revised within 2/3 years of publication.

Therefore, specification tables are given to illustrate the detailed nature of a respective sequence. These details are commented upon in the context of the developments driving the detail. They are also used to illustrate the evolution of the respective sequences so that future changes can be understood. Detailed footnotes have been omitted, these can be seen on the respective web sites.

17.2 The United States/North America Tripartite System

17.2.1 The Society of Automotive Engineers (SAE) Viscosity Classification

The first engine lubricant property classification was the SAE (Society of Automotive Engineers) J300 viscosity classification. This has evolved into a multigrade lubricant classification which indicates viscosity at both low (engine winter starting) temperatures and high (operating) temperatures for the 90% of the market which are multigrade lubricants. Respective viscosities are indicated by two numbers, the low-temperature viscosity is indicated with –W-(for Winter) and is given first, the second value shows the minimum kinematic viscosity at 100°C, together as SAE xxW-yy, e.g. SAE 10W-30.

Whereas initially low-temperature viscosities were extrapolated from measurements at higher temperatures, low-temperature cranking viscosity and pumpability are now measured by the Cold Cranking Simulator, ASTM D5293, and Mini-Rotary Viscometer, ASTM D4684, respectively. Kinematic viscosities at 100°C are measured by a very accurate capillary viscometer, ASTM D445. The high-temperature/high-shear (HTHS) viscosity measurement at 10^6 reciprocal seconds (s^{-1}) and 150°C, ASTM D4683 (CEC L 36-90-A, ASTM D4741 or ASTM D5481) is now recognised as being more representative of the lubricant conditions operating in modern vehicle bearings. It is now included in SAE J300 for SAE 20 and above. SAE viscosity grades effective from May 2008 for engine oils are given in Table 17.4.

Table 17.4 SAE viscosity grades for engine oils

SAE viscosity grade	Low-temperature,°C, cranking viscosity[1], mPa-s, maximum	Low-temperature,°C, pumping viscosity[2], mPa-s, maximum, with no yield stress[4]	Low-shear rate kinematic viscosity[3] mm^2/s at 100°C maximum/minimum	High-shear rate viscosity[4], mPa-s at 150°C, minimum
0W	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	13,000 at –10	60,000 at –15	9.3/–	–
20	–	–	5.6/<9.3	2.6
30	–	–	9.3/<12.5	2.9
40	–	–	12.5/<16.3	3.5 (0W-40, 5W-40, 10W-40 grades)
40	–	–	12.5/<16.3	3.7 (15W-40, 20W-40, 25W-40, 40 grades)
50	–	–	16.3/<21.9	3.7
60	–	–	21.9/<26.1	3.7

[1] By ASTM D5293; [2] by ASTM D4684 – note that the presence of any yield stress detectable by this method constitutes a failure regardless of viscosity; [3] by ASTM D445; [4] by ASTM D4683, CEC L-36-90 (ASTM D4741) or ASTM D5481

From SAE J300, revised 11/07, with effect from 05/2008, supersedes SAE J300 of 05/2004

17.2.2 Performance Classifications and the 'Tripartite'

The most influential world organisation defining and developing automotive lubricant qualities was the informal tripartite group of three large US organisations, SAE, ASTM ('American Society for Testing & Materials') and the American Petroleum Institute (API). Each organisation, with other interests beyond automotive lubricants, collaborated for many years, each with its defined role. The problem was that individuals and companies were often represented on two, or even all three, of the organisations.

As engine ratings increased, a lubricant classification was needed and API introduced the ML, MM and MS system for various early 1950s spark ignition engine operation service condition and an analogous DG, DM and DS system for diesel engines. No performance standards were initially specified: therefore the system was of limited utility, particularly as manufacturers tended to classify their products at the higher performance level. ASTM 'sequence tests' were then introduced as more precise definitions of oil performance and engine service, API cooperating with ASTM and SAE in 1969–1970 to establish new engine service classifications for lubricants where:

- ASTM defined the test methods and performance targets,
- API developed the service letter designations and 'user' language and
- SAE defined the need and combined the information into an SAE 'Recommended Practice' in the SAE Handbook for consumer use.

The current document is the 'Engine Oil Performance and Engine Service Classification' (other than 'Energy Conserving'), SAE J183 JUN91,(5). API Engine Service Classifications divide into the 'S-' lubricants series for passenger cars/light trucks (gasoline engines) and 'C-' lubricants series for commercial, farm, construction and off-highway vehicles (diesel engines). Lubricants can meet more than one classification, e.g. API SG/CD or CE/SG, thus the API SG category was formally adopted in 1988, similarly the API CE category was adopted in 1988 and recommended by all American heavy duty engine manufacturers. Heavy duty diesel engine specifications have been revised approximately every 4 years since API CF-4 in 1990 up to API CJ-4 in 2006, the heavy duty diesel engine specification current for four-stroke diesel engines at the time of writing. Similarly API SM is the present passenger car engine test category. The API system is described in 'Engine Service Classification and Guide to Crankcase Oil Selection', API Bulletin 1509, in its current technical bulletins.

API is not an approval body but certifies lubricant quality, developing its 'Service Symbol' (Fig. 17.1) in 1983, issuing licenses to oil companies for promotion of their lubricants. The symbol's centre circle shows the lubricant SAE viscosity grade, the outer ring upper half contains the API performance classification (only current performance qualities shown, obsolete performance levels may not be used). The outer ring lower half indicates an 'energy-conserving' or fuel economy standard. API's role has developed into its ‘engine oil licensing and certification system’ (EOLCS), discussed later in this section.

Fig. 17.1 The API service symbol

17.2.3 *The US Military and the SAE Lubricants Review Institute (LRI)*

Lubricant manufacturers worldwide required their products be approved to the US military MIL-L-2104, and subsequent MIL-L-46152, specifications. Few of these approvals were for their ostensible primary purpose of US military supply tendering, the military approval process itself was of considerable value to the lubricants industry due to its stringently objective reviewing procedure.

In 1977, approvals were placed with the SAE as the ‘Lubricants Review Committee’ of the Lubricants Review Institute (LRI), and this worked well for a decade. Engine lubricant test policy changes and strengthened API classifications, described below, gave lubricant companies and also end users more confidence, reducing the need for US military approvals. The influence of the LRI diminished, and the US military questioned the approval process cost-effectiveness and whether it should source lubricants at the appropriate API quality as a ‘commercial item description’ instead.

17.2.4 *Changes in the 1980s*

The SAE, API and ASTM ‘tripartite’ arrangement gave the United States an established lead in engine lubricant quality standards for many years but various concerns arose in the 1980s which led to change. The ‘tripartite’ constitutional framework eventually became both a virtue and a weakness, for relevant SAE and ASTM committees include automotive, lubricant and additive industry representatives who might have conflicting organisational objectives.

The Motor Vehicle Manufacturers Association, MVMA, proposed a new approach because new tripartite system lubricant specifications took 6/8 years from proposal to agreement with the final performance requirements often being lower than intended at the outset of such protracted programmes. This was both slow and unacceptable, particularly when set against a rapid rate of change in the automotive industry with MVMA's new technologies such as computer-aided design/computer-aided manufacturer, CAD/CAM, reducing new model development from 7 down to 3/4 years, now even shorter. MVMA was also concerned for the requirement to produce failure evidence, colloquially 'a basket of failed parts', before action was taken by the lubricant industry. MVMA argued for a changed approach, to 'prevent failure' rather than 'cure problems' and to allow lubricant development to meet future standards with future engines. A further problem was no defined field experience. The situation came to a head in 1989/1990 when the OEMs unilaterally proposed to develop their own specifications and approvals. The API argued that the existing system worked well for users with few or no significant field problems. It also argued that the industry sold lubricants to users with legal product liability and therefore, they must make a major contribution to the definition of product quality for their brand names. Both industries made significant concessions to resolve their differences.

17.2.5 American Chemistry Council, ACC, 'Code of Practice'

Parallel to the very slow pace of the 'tripartite' process, criticisms were also made of the definitions of 'passing' for lubricant quality tests. Essentially, should 'pass' mean 'always able to pass', or the 'capability to pass has been demonstrated', or an intermediate position? – this is more than semantics, for when the poor precision of engine tests compared to laboratory bench tests is considered, the answer is not self-evident. There was no requirement to pass each test every time or even on average, the exception being UK MoD approvals always requiring the test sponsor/laboratory to state their intentions and formulations before an engine test and to supply all results, pass or fail. Attempts to obtain a 'pass' for a particular formulation were strictly limited to two. Other specifying and approval authorities had normally not required such information, including the much more influential US military together with individual OEMs where it was not necessary to report failed results. Only passing results, usually with relevant engine components, must be presented. The limit of only two engine lubricant tests is particularly restrictive if the test concerned is:

- imprecise or 'bouncy',
- large business volumes are at stake, needing a price competitive formulation,
- a new formulation has already had a lot of resource spent on it and
- the particular (failed) test was close to the end of a long test sequence and reformulation to pass that test would be take too much time or expense.

Incentives to undertake multiple engine lubricant tests are considerable, limited in practice by the time for testing and the considerable costs entailed. This approach can approve a formulation, which might not pass all tests first time at random against specification, an unsatisfactory position. For some circumstances, lubricant formulators could make multiple attempts at each engine test within a specification. Another concern is lubricant formulation where high-quality internationally branded lubricant specifications may need up to 20 engine tests, together with bench tests, all with conflicting formulation needs. It may be difficult for a formulator to get new formulation approval at the first attempt and unreasonable to recommence testing because a small change has been made to one component's concentration in a formulation. But what is then 'reasonable' in formally handling changes to formulation? Some agreed practices are established for United States and Europe to allow controlled 'running changes' in a formulation under test, e.g.:

- US formulators follow the ACC Code of Practice and a running change in a formulation could be accepted without retesting or could require several tests to be repeated, thus as examples:
  - an increase in ashless dispersant level normally has a positive effect on sludge performance, yet neutral in other tests,
  - but increased mono-functional viscosity modifier would be detrimental to diesel engine piston deposit control.

Base stock composition changes are not usually made without invalidating approvals. Some base oil suppliers demonstrated interchangeability of base stock sources, others regard this as unnecessary, making their own judgements on base stock change validity. Different judgments have been made on the need to disclose formulation changes by different formulating companies. Judgements to disclose within an international company can be different for the geographical locations of approval authorities and also the experience and character of a company's continental operation.

Another pressure for change in the 1980s, separate from MVMA concerns, was the very strong growth of 'quality procedures' resulting partly from the success of Japanese industry and ISO 9000-series quality accreditation. This caused fresh concerns about industrial lubricant formulation/testing practices. These views were strongly argued at the 1989 CEC Symposium and drew serious interest in Europe. The additives industry supported these concerns and established a (US) Chemical Manufacturers Association (CMA) panel to write the 'CMA Product Approval Code of Practice', implemented in 1992, which originally covered the engine tests in the latest API 'S' category. In principle, other tests showing sufficient precision and control could be added. The five main features of the ACC Product Approval Code of Practice are:

1. Engine tests, registered with independent monitoring agencies prior to running, are only run on 'referenced (test) stands' with established, accepted, statistical criteria.

2. Sponsors select the testing laboratory but not the individual test stand which must normally be the ‘next available’ stand.
3. MTAC, as ‘Multiple Test Acceptance’ criteria, were introduced, where a lubricant must pass all controlled individual parameters on its first test. If a second test is needed, then each mean parameter value must be a pass. For running three or more tests, one complete test can be discarded and the mean parameter values from the remaining tests must pass. From experience, individual test results can be adjusted for identified severity changes in the test procedure from the lubricant test monitoring system using ASTM test monitoring centre control charting.
4. Details of changes to original formulations made as ‘minor’ formulation modifications were documented in great detail. Now all users of the code had a consistent set of working rules.
5. A ‘candidate data package’ provides all of the test results together with an audit trail to demonstrate the nature and validity of formulation changes, plus details of all scheduled tests and severity changes.

The Code of Practice is voluntary but all major players have committed to all tests initiated by them, and covered by the Code, are conducted in accordance with it.

17.2.6 EOLCS – The API Engine Oil Licensing and Certification System

EOLCS, the (API) engine oil licensing and certification system, arose from the problems and conflicts previously described, and has five key elements:

1. Defined performance standards defined similarly to the ‘tripartite’ system, where SAE, API and ASTM perform their previous traditional roles. If ASTM cannot achieve consensus, there is provision for ILSAC to take over. The system defines physical, chemical and performance characteristics of engine lubricants for API ‘SX’ and ‘CX’ specifications.
2. Engine test protocol requires that each engine lubricant test must be run according to the American Chemistry Council Code of Practice. Whilst use of the code is generally voluntary, EOLCS mandates its use if the particular test has been covered by the Code. In 2005 the tests covered were Sequences IIIF, IIIG, IIIGA, IVA, VG, VIB, VIII; Caterpillar 1 K, 1MPC, 1 N, 1P, 1R, C13; Mack T-8, T-8E, T-10, T-11, T-12; RFWT; Cummins M11, M11 EGR, ISB, ISM; Detroit Diesel 6V92TA. Refer to the latest ACC Code of Practice at: http://www.americanchemistry.com/sacc/bin.asp?CID=368DID=1361DOC=FILE.PDF).
3. A licensing procedure where lubricant marketers are responsible for product performance and must certify that each viscosity grade of each brand meets requirements. Detailed rules allow for base stock interchange and engine test read across in certain circumstances from one viscosity grade to another.

This is described in API 1509, the latest edition of which can be found at: http://www.api.org/certifications/engineoil/pubs/upload/150916thedition042007.pdf.

A sliding scale of fees, minimum $500/grade/company, with an extra $1000 for each 1 M (US) gallons sold above the first 1 M gallons (3.6 M l). The EOLCS minimum royalty fee for licensure is $1,050 US for API members and $1,250 US for non-members. Additionally, an annual fee of $0.0015 per gallon of licensed motor oil after the first million gallons production of licensed oil will be assessed, the latest on EOLCS at: http://www.api.org/certifications/engineoil/index.cfm.

4. Certification marks, two licensed marks were available:
   First, the API symbol (Fig. 17.1), previously, which can be anywhere on the packaging, with product details changing according to product nature and performance levels; second, the API certification mark, (Fig. 17.2), previously known as the ILSAC certification mark, which must be on the front of the container. This mark cannot be changed and can only be used if the product meets the current ILSAC performance level. If the product has the testing qualifications, the marketing organisations can use either or both symbols.
5. Conformance audits applied to all licensed products. Manufacturers whose lubricants fail can be subject to enforcement penalties which range from licence suspension to removal of the product from sale.

Fig. 17.2 The API certification

17.2.7 Laboratory Petrol/Gasoline Engine Test Development

Automotive engine manufacturers test their products on ‘test beds/stands’ for the further development of engines and provenance of their product. Caterpillar, as described previously, evaluated lubricants and additives using the 1930s L-1 engine tests and the L-4 (1942) petrol/gasoline Chevrolet engine test evaluated lubricants for oxidation and viscosity increase. These tests were the basis for a later proliferation of specification tests mainly using commercial, already extant, engine designs, usually the smaller versions.

Engine lubricant test development became very time consuming and even more expensive at the same time as doubts increased of their relevance to real field service, particularly for single cylinder engines. Emphasis moved towards commercial multi-cylinder engines of increasing size and complexity, parallel to commercial engine development. But larger engines require larger test beds and power absorption dynamometers, more fuel for longer periods and more time for rating/rebuilding than the previous smaller engines. Engine lubricant test evaluation costs have rapidly increased.

17.2.8 The API 'M' Series of Lubricants

As described in Section 17.2.3, automotive power and range developed steadily from the late 1940s/early 1950s into the 1960s. API defined a lubricant classification based on service use, the M-series of lubricants for light vehicles, ML (light duty), MM (medium duty) and MS (severe duty). MS grades assumed light vehicle operations with frequent low temperature, lightly stressed, short journeys mixed with occasional prolonged high temperature, long journeys. Different severities of lubricant grades were not specified and lubricant manufacturers/marketers decided which 'M' level applied for their product, hence as 'MS' was regarded as the 'best' grade, many lubricant formulations had this label irrespective of additive content or base lubricant suitability, which was unpredictable across brands.

US OEM engine tests defined 'MS' quality lubricants in 1962, mandatory for 1964 warranties. 'MS' lubricant engine tests successfully defined products with consistent oxidation resistance, wear performance, sludge formation and deposit control which were demonstrable under controlled test cell conditions, demonstrating standards rapidly accepted worldwide, using the original ASTM test sequences, Table 17.5. Europe added on some local manufacturer's engine tests to the US OEM engine test standards and requirements.

Table 17.5 The original MS quality test sequences

Sequence number	Purpose	Engine
I	Low temperature, medium speed scuffing	1960 Oldsmobile V8
II	Rust and corrosion at low temperatures	1960 Oldsmobile V8
III	Oxidation and deposits at high temperatures	1960 Oldsmobile V8
IV	Scuffing and wear	Chrysler V8 1962
V	Sludge at low and medium temperatures	1957 Ford Lincoln

The scuffing and wear aspects of Sequences I and IV were incorporated into Sequences III and V, thus I and IV were dropped and only Sequences II, III and V remained in (upwardly revised) severe forms, together with Sequence VI for energy efficiency. IV has re-appeared, as also has a Sequence VIII.

The ASTM sequence series, and their subsequent developments, have responded to rapidly increasing requirements of overall petrol/gasoline and diesel engine performance as increased energy densities, reduced emissions, increased fuel economy and considerably extended service intervals.

17.2.9 Evolution of the API 'SX/CX' – Standard Series

External requirements of emission control technology, higher energy densities and operating temperatures, increased fuel economy and extended service intervals stretched the newly established engine lubricant standards. The first automotive emission control device, the positive crankcase valve, PCV, recirculated internal engine blowby as partially burned reactive fuel substances. Lubricants were degraded more quickly and in ways which were potentially more difficult to treat. Contemporary MS level lubricant quality was increased, various OEMs set their increased standards and the sequence tests were revised with additional letters attached, such as II-B, III-B, V-B. Whilst developed for a wide range of service conditions, these tests were inadequate for high-speed, high-load service such as towing caravans and boat trailers for long distances and a new approach was needed.

The tripartite API, SAE and ASTM jointly introduced a robust new classification system, SAE J183, in 1970 to be readily extended or 'open ended'. Gasoline/petrol lubricants are 'S-(X)' prefixed, grafted onto the 'M' series through 'MS' quality levels equivalent to 'SD', with 'C-(X)' series as parallel diesel engine lubricants. The system has worked through formulation revisions to meet enhanced performance standards, through to the SM (2004) API engine oil classifications for service-fill oils, the latest classifications being on http://www.api.org/certifications/engineoil/categories/upload/EngineOilGuide2006.pdf. The progressive system has developed to meet increased technical demands of internal combustion engines where formulations are adjusted, rebalanced and improved to meet increased engine technology development. The issues have been to meet increased anti-oxidation standards, reduced sludge formation, reduced wear, maintenance of viscosity/viscosity indices, and reduced evaporative loss, a relentless increase in lubricant quality, a historical account of API SX from 'SA' to 'SJ' is given in Ref. [1].

Similarly, successive diesel 'C-(X)' standards have improved to meet higher energy densities, turbocharging, reduced piston deposits, lubricant consumption, bore wear and 'bore polish' and black sludge formation, through to the 'CJ-4' series in 2006. Standards initially changed to meet the use of higher fuel sulphur content, >0.5%, whereas more recent fuel developments have moved towards very much reduced levels of sulphur. Lubricant formulations have contributed to vehicle economy (US CAFE, Corporate Average Fuel Economy), ILSAC established energy-conserving lubricant standards for all engines that may claim API EC, principally addressed by the ASTM VI sequence fuel economy engine test.

The additive % mass in lubricant formulations, including VII, pour point depressants and anti-foam agents, can total up to 20% of the total mass. 'SX' petrol/gasoline progressions have encompassed increased lubricant service change intervals, the trend levelled in the mid-1990s but more recent developments show a further increase up to 50 k km (or 32.5 k miles) in some cases in Europe, with further increases to be expected, as:

- a steady increase in additive % total mass in formulations, but constrained by the need for reduced 'SAPS',
- rise, fall and then rise again of metal sulphonate, disappearance of thiophosphonate and the decline in phenate detergents, then the move towards 'Low SAPS',
- levelling off and then decline of ZDDP, and (later) increase 'other' anti-oxidants, to meet concerns for three-way catalytic converter fouling and an associated reduction in effective life,
- decline and omission of 'anti-rust',
- the continual increase in engine energy densities from 1949 and
- reductions in engine lubricant working volume and also consumption.

17.2.10 Achievements of the Tripartite System

The US tripartite system has made substantial achievements since its inception. It is striking that whilst dealing with and meeting the requirements described above, it has contributed *inter alia* towards decreasing lubricant consumption by 80% overall. In the same period average fuel consumption has also decreased by 43% and total lubricant consumption over a 15,000 km service interval has decreased by 92%. The US tripartite system has successfully responded to the initial challenge of specifying lubricant performance in vehicles; it has responded, and continues to respond by approximately 4-year reviews, to meet the additional requirements for lubricant performance specification introduced by environmental emission standards, particularly the low NO_x and soot standards. The increased soot levels resulting from changes in diesel engine combustion, together with increased service interval oil changes and with the further requirement of fuel economy, have led to problems of high-temperature deposits, ring sticking and oil thickening/dispersion. In turn, high soot levels can lead to increased valvetrain and bearing surface wear. These issues are addressed in the next subsections on the API CJ-4 and SM standards.

The API system, and similarly the ACEA system as will be seen in the next section, have worked well because, overall, an integrated approach has been taken involving developments in engine design, fuel and lubricant together. A range of lubricant specifications are available for a range of engines and fuels which have been developed over 10–20 years.

It is instructive to consider countries where such technical transitions have not been so well managed. For the largest national lubricant market in the Middle East [2], locally constructed vehicles are now complemented by more modern vehicles locally assembled by multi-national manufacturers to international standards, together with imported vehicles built to the same international standards. The problem is that high levels of impurities in fuels rapidly degrade predominantly obsolete lubricant formulations. Two-thirds of those lubricants for passenger car and light vehicles are API SC standard, declared obsolete by API a decade ago and not suitable for engines built after 1967. A further 26% of lubricants are graded SE, SF and SG, also declared obsolete and not suitable for vehicles constructed after 1979, 1988 and 1993, respectively. For heavy duty diesel trucks, 50% of lubricant volume is API CD (ca. 1955) and API CE (ca. 1985). Locally assembled European trucks and buses are very popular and require at least API CI-4 plus (ca. 2002). Locally manufactured light vehicles require at least API SL.

Fuel quality is the major problem, the official sulphur content of diesel is 10,000 ppm, i.e. 1%, probably higher in practice, whereas Europe and North America either have capped, or will shortly cap, diesel sulphur content at 10–20 ppm. The very high sulphur fuel degrades lubricants very quickly so that service interval lubricant drains for trucks average 4500 km (cf. 30,000–160,000 km in Europe) and 2000/2500 km for passenger and light vehicles (cf. 25,000 km in Europe). These fuel quality levels are particularly active in degrading low SAPS oils, as for API SM. In addition to sulphur, fuels also contain high levels of phosphorus which deactivate the three-way catalytic converters of new vehicles within their first hour, or so, of operation.

17.2.11 API C-(Series) Specifications for Heavy Duty Diesel Engines, Through to API CJ-4

The API C-series specifications have evolved as:
Now obsolete

CA/B/C: for naturally aspirated engines built up to 1959, 1961, 1990, respectively,
CD: introduced 1955 for certain naturally aspirated and turbocharged engines,
CD-II: introduced 1985 for two-stroke cycle engines and
CE: introduced 1985 for high-speed, naturally aspirated and turbocharged engines. Can replace CC and CD lubricants.

Current

CF: 1994, for off-road, indirect-injection and other diesel engines including those using fuel containing >0.5% sulphur. Can replace CD lubricants.
CF-2: 1994, for severe duty two-stroke engines, can replace CD-II lubricants.
CF-4: 1990, for high-speed, four-stroke, naturally aspirated and turbocharged engines, can replace CD and CE lubricants.
CG-4: 1995, for severe duty, high-speed, four-stroke engines using fuel containing <0.5% sulphur. Required for 1994 emission standards, can replace CD, CE and CF-4 lubricants.
CH-4: 1998, for high-speed, four-stroke engines designed to meet 1998 emission standards. Specifically formulated for fuel containing up to 0.5% sulphur w/w. Can replace CD, CE, CF-4 and CG-4 lubricants.

CI-4: 2002, for high-speed, four-stroke engines designed to meet 2004 emission standards implemented in 2002. Formulated to sustain engine durability where exhaust gas recirculation, EGR, is used. Some CI-4 lubricants may qualify for CI-4 PLUS status. Intended for fuels containing up to 0.5% sulphur. Can replace CD, CE, CF-4 and CG-4 lubricants.

CJ-4: 2006, for high-speed, four-stroke engines designed to meet 2007 emission standards. Formulated for use with fuel containing up to 0.05% sulphur (500 ppm w/w). Use of these lubricants with fuels with >15 ppm sulphur (0.0015% w/w) may affect the durability of exhaust after-treatment systems and/or oil drain service intervals. These lubricants will sustain emission control systems using particulate filters and other advanced after-treatments. Optimum protection for catalyst poisoning, particulate filter blocking, engine wear, piston deposits, low- and high-temperature stability, soot handling, oxidative thickening, foaming and viscosity loss due to shear. These lubricants exceed the performance criteria of CI-4, CI-4 PLUS, CH-4, CG-4 and can effectively lubricate engines requiring these API service categories. But, when using CJ-4 lubricants with fuel >15 ppm w/w sulphur, consult the OEM for service interval.

CK-4: Possibly to be expected at, or after, 2010. Emission-related issues may have reached their technical limits but the impact of bio-fuels on lubricants will become a separate issue, to be seen.

‘Obsolete’ lubricant grades are still available from specialist manufacturers for older, perhaps ‘classic’ vehicles. For ‘current’ grades, it is self-evident from the sequence of outline requirements set out above that the major influence driving their recent development has been the effects of decreased fuel sulphur content and the requirements of the various forms of emission control systems.

17.2.12 The API CJ-4 Heavy Duty Diesel Engine Specification

The API CJ-4 specification for heavy duty diesel lubricants has two sections, first for laboratory tests, second for engine tests, set out in Table 17.6.

The purpose of the CJ-4 laboratory tests are:

1.1 *Viscosity Grades*: from Table 17.2, giving lubricant manufacturers freedom to develop ‘lighter grades’, such as the 0 W-20 developed for truck fuel economy [2].

1.2 *High-Temperature Corrosion Bench Test at 135°C*: measuring increased corrosion by used oils of common metals in engines, e.g. copper and lead, from increased operating temperatures.

1.3 *Foaming*: to measure the foaming tendency of the candidate lubricant formulations.

1.4 and 1.6, *Shear Stability*: first, the ability of the lubricant to maintain its 100°C viscosity after 90 passes by ASTM D7109; second, its ability to maintain a minimum 3.5 cP viscosity at 150°C after the high-temperature/high-shear test, as in SAE J300.

Table 17.6 Heavy duty diesel engine category for API CJ-4

(i) Laboratory tests for API CJ-4

				Limits		
Requirement	Test method	Properties	Unit	One test	Two tests	Three tests
1.1 Viscosity grades		SAE J300		Manufacturer specifies viscosity within SAE J300 specification		
1.2 High-temperature corrosion bench test	ASTM 6594	Copper in used oil increase, max	ppm	20	No MTAC	
		Lead in used oil increase, max	ppm	120		
		Copper strip rating, max	–	30		
1.3 Foaming	ASTM D892	Foaming/settling, max				
		Sequence I	%	10/0	No MTAC	
		Sequence II	%	20/0		
		Sequence III	%	30/0		
1.4 Shear stability	ASTM D7109	KV at 100°C after 90 passes for XW-40, min	cSt	12.5	No MTAC	
		KV at 100°C after 90 passes for XW-30, min	cSt	9.3		
1.5 Noack volatility	ASTM 5800	Evap loss at 250°C, Viscosity grades other than 10W-30, max	%	13	No MTAC	
		Evap loss at 250°C, 10W-30, max	%	15		
1.6 High temperature/high shear	ASTM D4883	Viscosity at 150°C	cP	3.5	No MTAC	
1.7 Sooted oil MRV	ASTM D6896	180 h sample from Mack T-11 or T-11A	cP	25,000	No MTAC	
			Pa	<35		
1.8 Chemical limits (non-critical)		Viscosity at –20°C, max				
		Yield stress				
	ASTM D874	Sulphated ash, max	%	1.0	No MTAC	
	ASTM D4951	Phosphorus, max	%	0.12		
		Sulphur, max	%	0.4		
1.9 Seal compatibility	ASTM D7216	**Volume change**	**Hardness**	**Tensile strength**	**Elongation**	
	Nitrile	+5/–3	+7/–5	+10/–TMC1006	+10/–TMC1006	
	Silicone	+TMC1006/–3	+5/–TMC1006	+10/–45	+20/–30	
	Polyacrylate	+5/–3	+8/–5	+18/–45	+10/–35	
	FKM	+5/–2	+7/–5	+10/–TMC1006	+10/–TMC1006	
	Vamac G	+TMC1006/–3	+5/–TMC1006	+10/–TMC1006	+10/–TMC1006	

Table 17.6 (continued)

(ii) Engine tests for CJ-4

				Limits		
Requirement	Test method	Properties	Unit	One test	Two tests	Three tests
2.1 Mack T-11	ASTM 7156	Soot at 4 cSt inc, min	%	3.5	3.4	3.3
		Soot at 12 cSt inc, min	%	6.0	5.9	5.9
		Soot at 15 cSt inc, min	%	6.7	6.6	6.5
2.2 Mack T-12		Merits, min		1000	1000	1000
2.3 Cummins ISB		Tappet wear, max	mg	100	108	112
		Cam wear, max	microns	55	59	61
		Crosshead weight loss	mg	Rate/report	Rate/report	Rate/report
2.4 Cummins ISM		Merits, min	mg	1000	1000	1000
		Top ring weight loss, max		100	100	100
2.5 Caterpillar 1 N	ASTM 6750	Top land heavy carbon, max	%	3	4	5
		Top groove fill	%	20	23	25
		Weighted demerits, max	demerits	286.2	311.7	323.0
		Average oil consumption (0–252 h), max	g/kW h	0.5	0.5	0.5
		Ring/liner scuffing		None	None	None
2.6 Caterpillar C13		Merits, min		1000	1000	1000
		Hot stuck rings		None	None	None
2.7 Engine oil aeration	ASTM 6894	Oil aeration volume, max	%	8.0 (MTAC)	8.0 (MTAC)	8.0 (MTAC)
2.8 Roller follower wear test	ASTM 5966	Roller follower pin wear, max	microns	7.6	8.4	9.1
2.9 Sequence IIIF	ASTM 6984	Viscosity Inc. at EOT, max	%	275 MTAC	275 MTAC	275 MTAC

1.5 *Volatility*: measures evaporative loss by the Noack test, or its simulation, limited to 13% (15% for lighter grades), reflecting the tightened limits since first introduced in API CH-4 of 15–20%, according to grade.

1.7 *Sooted Oil Maximum Relative Viscosity*: to measure the viscosity and yield stress at –20°C of used lubricants from a 180 h Mack T-11/11A test. An increased requirement from API CI-4 for a 75 h sample from (a less severe) Mack T-10 test.

1.8 *Chemical Limits*: a new limit test introduced into API CI-4 for sulphated ash, phosphorus and sulphur, for ‘Low SAPS’.

1.9 *Seal Compatibility*: essentially the same as for API CH-4, when it was introduced but with an extended material test range.

The purpose of the API CJ-4 engine tests are:

2.1 *Mack T-11*: to generate a substantially sooted lubricant sample, for viscosity limit measurements up to 6.7%, from this severe engine test.
2.2 *Mack T-12*: merit rating of components for deposit control.
2.3 *Cummins ISB*: a new engine test in API CJ-4, to measure tappet, cam and crosshead component wear, partially replaces the Cummins M-11-EGR test in API CI-4 and CH-4.
2.4 *Cummins ISM*: a new engine test in API CJ-4, for merit rating of deposit control and top ring weight loss, as a measure of wear.
2.5 *Caterpillar 1N*: a continuation of the Caterpillar 1MPC, 1P, 1 K and 1R tests used in successive API C- tests since API CF-CF-2, for the measurement of deposits and wear through top land heavy carbon, top groove fill (by deposits), weighted demerits, average oil consumption and ring/liner scuffing.
2.6 *Caterpillar C13*: a new engine test for the measurements of deposit 'merits' and 'hot stuck rings'.
2.7 *Engine Oil Aeration*: an engine test which complements the laboratory 1.3 'foaming test'.
2.8 *Roller Follower Wear Test*: a long established wear test since API CG-4.
2.9 *Sequence IIIF*: measures viscosity at end of test, 275%, slightly tighter than 295% max at 60 h for API CH-4, different emphasis from 67.5 minimum hours to 375% increase in viscosity in API CG-4.

This comparative commentary of the heavy duty diesel engine test category for API CI-4 shows that successive test categories gradually revise both the nature of the tests, either as bench tests or engines and also the passing limits for these tests. This evolutionary process is expected to continue with the 'API CK-' series when the CI- series is revised.

Viewing these test requirements in the context of previous heavy duty diesel engine test categories, from API CG-4 through to API CJ-4, the increasing number of tests for each successive specification becomes evident, Table 17.7. New tests, or versions of tests, are included into the new specifications and the test engines, or their regimes used, are revised or replaced to respond to the perceived new issues.

In addition, the 'properties' column becomes divided into sub-categories and the 'limits set' decrease, the test for the soot-induced thickening of the lubricant changes in several parameters, Table 17.8. The engine test becomes progressively more severe, from the Mack T-8 to the Mack T-11. At the same time, as an example, the viscosity properties for each specification become more differentiated, from:

- a viscosity increase at 3.8%, max, of 11.5 cSt for one test for CG-4 by ASTM 5967 and
- through to increases of 3.5, 6.0 and 6.7% soot for viscosities at 4, 12 and 15 cSt for one test of CJ-4 by ASTM 7156.

Table 17.7 Changes in requirements through API CG-4 to API CJ-4

CJ-4, 2006	CI-4 and CI-4 PLUS, 2002	CH-4, 1998	CG-4, 1995
Laboratory tests			
1.1 Viscosity grades	1.1 Viscosity grades	1.1 Viscosity grades	1.1 Viscosity grades
1.2 High-temperature corrosion, 135°C	1.2 High-temperature corrosion bench test	1.2 High-temperature corrosion bench test	1.2 Cummins bench corrosion test
1.3 Foaming	1.3 Foam test	1.3 Foam test	1.3 Foam test
1.4 Shear stability	1.4 Shear stability	1.4 Shear stability	
1.5 Noack volatility	1.5 Noack volatility	1.5 Volatility	
1.6 High temperature/high shear	1.6 High temperature/high shear		
1.7 Sooted oil MRV	1.7 Low-temperature pumpability		
1.8 Chemical limits	Elastomer compatibility		
1.9 Seal compatibility			
Engine tests			
2.1 Mack T-11	2.1 Mack T-8E	2.1 Mack T-8E	2.1 Mack T-8
2.2 Mack T-12	2.2 Mack T-10	2.2 Mack T-9	2.2 Caterpillar 1 N
2.3 Cummins ISB	2.3 Cummins M11-EGR	2.3 Cummins M-11	2.3 Roller follower wear test
2.4 Cummins ISM	2.4 Caterpillar 1R	2.4 Caterpillar 1-P	2.4 Sequence IIIE
2.5 Caterpillar 1 N	2.5 Caterpillar 1 K or 1 N	2.5 Caterpillar 1-K	2.5 CRC L-38
2.6 Caterpillar C13	2.6 Roller follower wear test	2.6 Roller follower wear test	2.6 HEUI air entrainment test
2.7 Engine oil aeration	2.7 Engine oil aeration test	2.7 Engine oil aeration test	
2.8 Roller follower wear test	2.8 Sequence IIIF	2.8 Sequence IIIF	
2.9 Sequence IIIF			

Table 17.8 Changes in soot loading viscosity tests, CG-4 to CJ-4

Test	Requirement	Test method	Properties	Unit	Limit		
					One test	Two tests	Three tests
CJ-4	Mack T-11	ASTM D7156	Soot at 4 cSt inc, min	%	3.5	3.4	3.3
			Soot at 12 cSt inc, min	%	6.0	5.9	5.9
			Soot at 15 cSt inc, min	%	6.7	6.6	6.5
CI-4	Mack T-8E	ASTM D5967	Relative viscosity at 4.8% soot, max (RV=viscosity at 4.8% soot/viscosity of new oil sheared in D6278		1.8	1.9	2.0
CH-4	Mack T-8E	ASTM 5967-96 Ext	Relative viscosity at 4.8%, max	cSt	2.1	2.2	2.3
			Viscosity increase at 3.8%, max	cSt	11.5	12.5	13.0
CG-4	Mack T-8	ASTM 5967	Viscosity increase at 3.8%, max	cSt	11.5	12.5	13.0
			Filter plugging, differential	kPa/psi	138/20	138/20	138/20
			pressure, max	g/kWh/lb/bhp.h	0.304	0.304	0.304
			Oil consumption, max		0.0005	0.0005	0.0005

17.2.13 The Passenger Car Engine Test Category for API SM

The petrol passenger car API specifications (also including light vehicles such as vans and mini-buses) have evolved through:

Obsolete

SA for engines built up to 1930, contains no additives; SB for engines built up to 1951; SC for engines built up to 1967; SD for engines built up to 1971; SE for engines built up to 1979 *(use of SA–SE lubricants can damage more modern equipment).*

SF: suitable for engines built up to 1988.
SG: suitable for engines built up to 1993.
SH: suitable for engines built up to 1996.

Current

SJ: for 2001 and older automotive engines.
(the ‘SI’ and ‘SK’ specifications were intentionally omitted by API)
SL: for 2004 and older automotive engines.
SM: for all automotive engines currently in use, introduced 2004, for improved oxidation resistance, improved deposit protection, better wear protection and better low-temperature performance of the service life of the lubricant. Some SM formulations may meet the latest ILSAC specification as ‘Energy Conserving’.

A characteristic of automotive petrol lubricant specifications is the inclusion of the performance properties of each previous category, thus the SM specification gives full protection for SJ or SL requirements. This differs from the diesel engine specifications which usually, but not necessarily, include the performance properties of earlier specifications, Table 17.9.

The API SM specification, set out in Table 17.9, has mainly similar aims to that of CJ-4. The differences are that the CJ-4 heavy duty diesel specification has a major pre-occupation with the effect of combustion soot-induced thickening of the oil arising from relatively recently introduced environmentally associated emission controls, whereas API SM uses the ASTM sequences IIIG and IIIGA to measure the ability of the lubricant formulation to withstand (mainly) oxidative thickening. Phosphorus and sulphur content limits of lubricant formulations are set. The major part of the API SM specification is concerned with in-cylinder component and valve gear wear.

17.2.14 Future Specifications

The next updates of the API SM (SN?) and CJ-4 (CK-4?) are to be reasonably expected in 2012. The new issues they will probably have to address are

Table 17.9 Passenger car engine test category for API SM

Requirements	Test method	Properties	Unit	Limits SM/EC GF4
Laboratory tests for API SM				
1.1 Viscosity grades		All those that apply, typically SAE 0W-20, 0W-30, 5W-20, 5W-30 and 10W-30		Manufacturer sets targets within SAE J300 specification
1.2 Foam test (Option A)	ASTM D892 ASTM D6082	Sequence I	ml initial, Foam, ml/ml after settling	10/0
		Sequence II		50/0
		Sequence III		10/0
		Sequence IV		100/0
1.3 Phosphorus	ASTM D4951	Phosphorus content	%	0.06 min, 0.08 max
1.4 EOFT	ASTM D6795	0.6% Water–dry ice–% reduction in flow	% reduction	50 max
1.5 EOWTT	ASTM D6794	With 0.6% water	% reduction	50 max
		with 1.0% water	% reduction	50 max
		with 2.0% water	% reduction	50 max
		with 3% water	% reduction	50 max
1.6 TEOST (MHT4)		Total deposits	Mg	35 max
1.7 Homogeneity and miscibility	ASTM D6922	Oil compatibility		Pass
1.8 Scanning brookfield	ASTM D5133	Gelation index		12 max
1.9 Volatility	ASTM D5800	Volatility (Noack)	% off at 250°C	15 max
	ASTM D6417	Volatility (GCD)	% off at 371°C	10 max
1.10 BRT	ASTM D6557	Rust rating	Average grey value	100 min
1.11 Sulphur	ASTM D4951 or D2622	Sulphur content of 0W and 5W multigrades	%	0.5 max
		Sulphur Content of 10W multigrades	%	0.7 max

Table 17.9 (continued)

Requirements	Test method	Properties	Unit	Limits SM/EC GF4
Engine tests for API SM				
2.1 Sequence IIIG		Viscosity increase of 100 h	% Merits	150 max
		Average weighted piston deposits	# µ	3.5 min
		Hot stuck rings		None
		Average cam plus lifter wear		60 max
2.2 Sequence IIIGA	ASTM D4684	Aged oil low-temperature viscosity	Cp	Meets requirements of original grade or the next higher grade
2.3 Sequence IVA	ASTM 6891	Cam wear average	µ	90 max
2.4 Sequence VG	ASTM 6593	Average engine sludge	Merits	7.8 min
		Rocker arm cover sludge	Merits	8.0 min
		Average piston skirt varnish	Merits	7.5 min
		Average engine varnish	Merits	8.9 min
		Oil screen clogging	%	20 max
		Hot stuck rings	#	None
		Cold stuck rings	#	Rate and report
		Oil ring clogging	%	Rate and report
		Follower pin wear, cyl #8 average	µ	Rate and report
		Ring gap increase, cyl 1 and 8, average	µ	Rate and report
		Oil screen debris	% area	Rate and report
2.5 Sequence VIII	ASTM 6709	Bearing weight loss	Mg	26 max
		10 h stripped viscosity	cSt	Stay in grade
2.6 Sequence VIB (Required for ILSAC GF-4 only)	ASTM 6837	SAE 0W-20 and 5W-20 grades	All %FE11/%FE12	2.3/2.0 min
		SAE 0W-30 and 5W-30 grades		1.8/1.5 min
		SAE 10W-30 and all other grades		1.1/0.8 min

Bio-fuels: the effects of the respective bio-fuels for petrol and diesel engines on lubricants. Use of vegetable-based diesel fuels or diesel fuels with various levels of vegetable oils such as 5 or 10% leads to fuel condensation/deposition in the sump of the engine and dilution of the lubricant by accumulation of the relatively low volatility vegetable oil. The vegetable oil-derived fuel dilution leads to an enhanced viscosity and also enhanced oxidation of the lubricant. One physical aspect of this fuel dilution effect is an increased lubricant volume which can be stirred into a foam by rotating big ends. A foamed lubricant gives very low protection of bearing surfaces and dramatically enhanced wear can result.

One hundred percent ethyl alcohol as a spark ignition engine fuel or alcohol substituted at low levels in petrol can interact with and cause problems with the additive pack in the current type of lubricant formulations. Reformulation of lubricants to deal with the effects of these fuels will be necessary. However, the relevant technology is available from South America where, for example, Brazil has operated light vehicles on total alcohol fuels for over a decade.

Efficiency Standards: the existing corporate average fuel efficiency, or CAFE, standards have improved fuel efficiency in the United States. These standards only apply to petrol-fuelled vehicles at present; the strongly competitive market for diesel engine efficiency appears not to need standards. At the end of the first decade of this century the urgency to improve petrol automotive energy efficiency was further emphasised by changes in government policy. Lubricants have a role in improving fuel efficiency through reduced friction loss in bearings, in-cylinder and valvetrain, possibly by formulating lower SAE grade products. This will require the development of higher fuel efficiency specifications as in API SM 2.6 and ILSAC.

17.3 ACEA – European Lubricant Specifications and Approvals

17.3.1 Individual Manufacturers

The ACEA system is as European as the API system is American and there are both similarities and contrasts between them. In contrast to the US tripartite specifications, Europe initially developed robust, single cylinder lubricant test methods using Petter-AV diesel and W-1 petrol engines, as originally designed for small construction vehicle/motive power for pump/electricity generation use, therefore cheap to buy and to rebuild. In addition, European OEMs have different relationships with lubricant suppliers than in the United States, and further, a different attitude towards lubricant classification and approval, e.g. the Daimler 'Betriebsstoff-Vorschriften/Specifications for Service Products (Fuels, Lubricants, etc.)', as regularly updated, are a comprehensive guide to the lubrication requirements for their vehicle products and components under a range of service conditions. Approved lubricants are listed, giving them considerable additional marketing value.

Whilst the need for individual OEM specifications/approvals has reduced in recent years because of the European ACEA (CCMC) classifications, and others, further OEM specifications/approvals remain and have become more important. Thus, Volkswagen (VW) initiated their own approvals, profoundly affecting other testing procedures by requiring all approval tests be done within a limited group of independent laboratories. These must produce tests for several reference lubricants which demonstrate adequate discrimination between them. Candidate test lubricant results are assessed against reference oil results obtained on the same test stand, VW arguing that these procedures enhance test quality. The initiatives taken by some engine manufacturers should benefit engine lubricants overall, engine development and, ultimately, vehicle owners.

17.3.2 CCMC, Now ACEA

CCMC, ‘Comité des Constructeurs du Marché Commun’ (‘Committee of Common Market Automobile Constructors’), was founded in 1972 as a trade association. ACEA, the ‘Association des Constructeurs Européens d’Automobiles’, replaced it in 1991 with a different organisational constitution.

CCMC crankcase lubricant sequence development was quite different from the US tripartite system because the EU motor industry developed plans privately, unrestricted by consensus with the lubricant industry. In response and anticipating the need for dialogue with CCMC, the Technical Committee of Petroleum Additive Manufacturers, ATC, was formed in 1974. Equally, a lubricant marketers organisation, Association Technique de l’Industrie Européene des Lubrifiants, ATIEL, was formed in 1976 for discussion with CCMC, then ACEA.

The first CCMC fuels and lubricants working group sequences were published in 1975 and covered additional requirements beyond the API designations. These necessary additional tests covered the differences of small engine operation in Europe, mostly developed by the Coordinating European Council for the Development of Performance Tests for Transportation Fuels, Lubricants and Other Fluids, CEC, from recommended engine manufacture prototype tests, extensively revised in 1984 and 1991. However, the internal tensions of CCMC led to its replacement by ACEA in 1996.

17.3.3 Differences Between CCMC/ACEA Categories and API Test Sequences

Whilst US classifications are backed directly by working groups monitoring test quality with only one recommended minimum quality for a specific application at any time, ACEA (previously CCMC) sequences are mainly based on CEC test procedures but with much less formal links between the organisations. Further, European classifications include a substantial diesel light vehicle market which does not exist in the United States. ACEA recognises the provision of different classifications of lubricants for the same equipment, dependent on service interval and is not involved in lubricant approvals, not wishing to incur development and maintenance costs for the necessary infrastructure. ACEA does not have legally enforceable powers, which is probably advantageous as it operates across a number of nation states, whereas the US system operates across one, integrated, state.

ACEA objectives are very similar to CCMC but with a different constitution. In addition to European manufacturers, it includes global (US) companies manufacturing in Europe, e.g. General Motors and Ford together with wider European companies, e.g. Volvo, Saab-Scania whose Scandinavian headquarters were outside the original EC (common market) but have since joined the European Union. ACEA issues ‘lubricant sequences’ but does not give approvals, continuing to favour wherever possible multi-cylinder European engine tests developed by CEC. ACEA has common sequences for gasoline and light duty diesel engines and also heavy duty diesel engines. Most recent developments have been the combination of the ‘B’ light diesel and ‘A’ petrol ACEA sequences to give the A/B sequences, driven by current developments in European light diesel engine technology and fuel composition.

17.3.4 CEC

CEC has a parallel, but much more limited, role in Europe than ASTM in the United States. Its scope is limited to performance tests on engines and rigs with bench tests left to other organisations such as:

- the Institute of Petroleum (IP), establishing IP methods or
- ‘Deutscher Normenausschuss’, awarding DIN (Deutsche Industrie Normen) classifications.

CEC develops tests but does not set limits, leaving them to be set by commercial organisations. Its senior body, the CEC Council, has members elected from its ten (original) constituent national European organisations, with several committees reporting to it, including the Engine Lubricants Technical Committee (ELTC) and the Transmission Lubricants Technical Committee (TLTC), each having voting membership from national organisations. Working groups report to their relevant committees and have members from individual companies. Only at the working level has CEC operational commonality with ASTM. CEC continues to be useful but the increasing rate of change has reviewed existing processes, as in the United States, the basic problems being that:

- decision making is slow, for council and technical committee meetings held every 6 months,
- voting by national bodies has strengths but also weaknesses, decisions made by members without the relevant detailed experience for effective judgment and
- many CEC lubricant engine test procedures are less rigorously defined and maintained than their US counterparts.

CEC recognised these issues and has done much in the last decade to improve practice, now cooperating closely with ACEA, ATIEL and ATC. An executive committee and a full-time technical director have accelerated technical decisions, encouraged new protocols for test procedures, resulting in new, high-quality tests.

17.3.5 Changes in the European Automotive Industry

To say that change is inevitable in Europe is rather wisdom after the event. Both the automotive industry and the oil industry have had major upheavals, mergers and rationalisations, generally as part of worldwide changes. The worldwide aspect of merger/changes/collaborations does call into question the relevance of national/continent-based standards with the emergence of global markets. Examples include:

- Daimler-Benz and Chrysler merged to become Daimler–Chrysler, a European/American business operating worldwide, with automotive production interests in Asia and the Pacific Rim countries, and then demerged to its initial constituent parts.
- Ford acquired Volvo (small vehicles), LandRover, Jaguar and Aston-Martin, then later sold Aston-Martin separately and then Jaguar/LandRover to Tata.
- BP merged with ARCO, Amoco and Castrol.
- Esso and Mobil merged to form Exxon–Mobil globally.
- Total, Petrofina and Elf merged to form Total.

Automotive production activity is now increasingly globalised, as are also the lubricant companies and their lubricant products, and also the additive companies. The ‘players’ are now global businesses with common issues to address, well beyond regional and national problems. Whilst European lubricant methods continue to evolve, they increasingly converge with United States and international practice. It is accepted that quality classifications cannot be developed and maintained on poor test procedures, therefore the initial focus was:

- to identify the most important bench, rig and engine test parameters and
- to develop new tests/improve existing CEC tests to far more exacting quality standards.

As individual test quality is improved, automotive, lubricant and additive industries have jointly developed the management of new performance specifications through the European Engine Lubricant Quality Management System (EELQMS). Where appropriate and practicable experience has been drawn from the United States. The ATC Code of Practice contains European tests and is aligned closely with the CMA Code, given in Section 17.2.5; similarly, ATIEL has a lubricant Code of Practice broadly based on API EOLCS, given in Section 17.2.6.

Auditing and quality monitoring has equally recognised importance in both Europe and the United States. Significant differences between United States and European practice are that Europe has a larger number of smaller, more diverse, laboratories placing more emphasis on ‘the laboratory’ as a whole through ISO 9000 quality systems/EN 45001 laboratory accreditation. The United States favours the ‘test stand’ approach.

ACEA replaced CCMC in 1991, its sequences came into force in 1996, replaced later by 1998 versions, encouraging high-quality testing protocols but essentially relying upon lubricant company integrity for ACEA quality claims. It has maintained a 2-year revision programme which merged the ‘A’ series light vehicle petrol and ‘B’ light vehicle diesel into the ‘A/B’ sequences in 2004, a ‘C’ category compatible with ‘after-treatment’ pollution control systems and the ‘E’ sequences for heavy duty diesel engines.

17.3.6 The ACEA ‘A/B’ and ‘C’ Gasoline/Diesel Light Vehicle Lubricants

The relationship between the A, B, A/B and C ACEA sequences is given in Fig. 17.3:

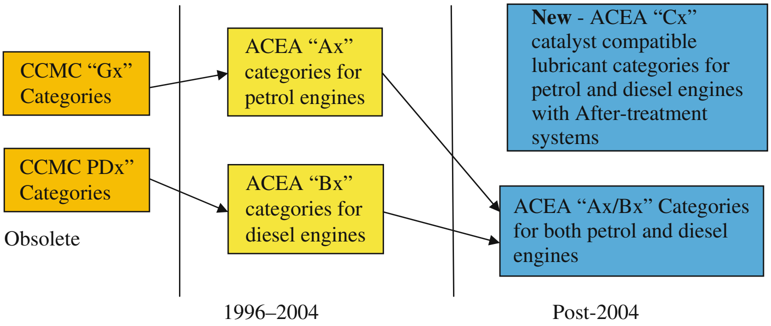

Fig. 17.3 Evolution of ACEA ‘A*x*’, ‘B*x*’, ‘A/B*x*’ and ‘C’ sequences ($x = 1, 2, 3$, etc.)

The ‘A/B’ petrol and diesel engine lubricant categories are all ‘stable, stay-in-grade’ lubricants and may be unsuitable for some engines, the owner manual/handbook should be consulted, where:

A1/B1: for extended drain intervals in petrol and diesel light vehicle (car and light van) engines, specifically designed for low-friction, low-viscosity lubricants. A high-temperature/high-shear rate viscosity of 2.6 mPa.s for xW-20 and 2.9–3.5 mPa.s for all other viscosity grades.

A3/B3: for high-performance petrol and diesel light vehicle engines and/or for extended drain intervals where specified by the engine manufacturer and/or for year-round use of low-viscosity lubricants, and/or for severe operating conditions as defined by the engine manufacturer.

A3/B4: intended for use in high-performance petrol and direct-injection diesel engines, but also suitable for applications described under A3/B3.

A6/B6: for use at extended drain intervals in high-performance petrol and diesel light vehicle engines designed for low-friction, low-viscosity lubricants with a high-temperature/high-shear rate viscosity of 2.9–3.5 mPa.s.

Laboratory and engine test requirements for ‘A/B’ and ‘C’ ACEA 2008 European Oil Sequence for petrol and diesel engine service-fill lubricants are defined in Table 17.10. A new engine test is introduced for the ‘A/B–08’ as the OM646LA, a light duty diesel engine test replacing the OM602A, for the purpose of giving increased wear protection. This test is also the first ACEA test to run on 5% biodiesel, known as BO5. This test is also introduced across the ‘C(X)-08’ and ‘E(X)-08’ series, described later in this section.

The ‘C’ catalyst compatible lubricant category was introduced in 2004 to be compatible with ‘after-use’ pollution control systems and are stable, stay-in-grade, catalyst compatible lubricants for diesel- and petrol-fuelled light vehicles:

C1 – with either diesel particulate filters, DPF, or petrol three-way catalysts, TWC, requiring low-friction, low-viscosity lubricants with HTHS minimum of 2.9 mPa.s. These lubricants will increase DPF and TWC life and maintain fuel economy. These lubricants have the lowest sulphated ash/phosphorus/sulphur (SAPS) limits.

C2 – for high-performance car and light van diesel and gasoline engines with either DPF and TWC, designed to use low-friction, low-viscosity oils with an HTHS viscosity higher than 2.9 mPa.s. These lubricants will increase diesel particulate filter/three-way catalyst operating lifetimes and maintain vehicle fuel economy.

C3 – for high-performance car and light van diesel/gasoline engines vehicles with DPF and TWC with a minimum HTHS viscosity higher than 3.5 mPa.s. These lubricants will increase DPF/TWC operational life.

C4 – for high-performance car and light van diesel/gasoline engines vehicles with DPF and TWC with a minimum HTHS viscosity greater than 3.5 mPa.s. These lubricants increase DPF/TWC operational life.

These lubricants may be unsuitable for some engines and the vehicle manual or handbook should be consulted.

ACEA ‘C’ sequence laboratory tests:

The laboratory ‘C(X) ’sequence requirements for 1.1, 1.2 and 1.10–12 are the same as for the ‘A/B’ sequences, the different requirements are set out in Table 17.11. Compared to the ‘A/B–08’ series, the ‘C–08’ requirements are:

- marginally more stringent for high-temperature viscosity and high-shear rate (1.3),
- 2% points less for evaporative loss (1.4),
- tighter limits for sulphur, phosphorus and sulphated ash (1.5–7), to protect the three-way catalyst and emission control system and
- lower TBN levels for C3- and C4-08, as a result of lower SAPS.

Table 17.10 'A/B-08' ACEA sequences

Laboratory tests							
				Limits			
Requirement	Test method	Properties	Unit	A1/B1-08	A3/B3-08	A3/B4-08	A5/B5-08
1.1 Viscosity grades		SAEJ300 latest active issue		No restriction except as defined by shear stability and HT/H8 requirements. Manufacturers may indicate specific viscosity requirements related to ambient temperature.			
1.2 Shear stability	CEC L-014-83 or ASTM D6278	100°C viscosity after 30 cycles	mm^2/s	XW-20 stay in grade, xW30 ≥ 9.3 xW40 ≥ 12.0	All grades to be stay in grade		
1.3 Viscosity at high-temperature and high-shear rate	CECL-036-90 (2nd Edition) (Ravenfield)	Viscosity at 150°C and $10^6 s^{-1}$ shear rate	mPa.s	≥2.9 and ≤3.5; Xw-20: 2.6 min	≥3.5	≥3.5	≥2.9 and ≤3.5
1.4 Evaporative loss	CECL-040-93 (Noack)	Max weight loss after 1 h at 290°C	%	≤15	≤13		
1.5 TBN	ASTM D2896		mgKOH/g	≥8.0			
1.6 Sulphated ash	ASTM D874		% m/m	≤1.3	≤1.5	≤1.5	≤1.6 (see note 2)
				Note that the following sections apply to all sequences			
1.7 Sulphur (see note l)	ASTM D5185		% m/m	Report			
1.8 Phosphorus (see note 1)	ASTM DS185		% m/m	Report			

Table 17.10 (continued)

Laboratory tests								
				Limits				
Requirement	Test method	Properties	Unit	A1/B1-08	A3/B3-08	A3/B4-08	A5/B5-08	
1.9 Chlorine	ASTM D6443		ppm m/m			Report		
1.10 Oil/elastomer compatibility	CECL-039-96 (see note 3)	Max variation of characteristics after immersion for 7 days in fresh oil without pre-ageing.		**Elastomer type** **REI**	**RE2-99**	**RE3-04**	**RE4**	**AEM VAMAC**
		Hardness DIDC	Points					
		Tensile strength	%	–1/+5	–5/+8	–22/+1	–5/+5	As per Daimler
		Elongation at rupture	%	–40/+10	–15/+18	–30/+10	–20/+10	
		Volume variation	%	–50/+10	–35/+10	–20/+10	–50/+10	
				–1/+8	–7/+5	–1/+22	–5/+5	
1.11 Foaming tendency	ASTM D892 without option A	Tendency stability	ml	Sequence I (24°C) 10 – nil Sequence II (94°C) 50 – nil Sequence III (24°C) 10 – nil				
1.12 High-temperature foaming tendency	ASTM D6082 High temperature foam test	Tendency stability	ml	Sequence IV (150°C) 100 – nil				

Table 17.10 (continued)

Engine tests							
				Limits			
Requirement	Test method	Properties	Unit	A1/B1-08	A3/B3-08	A3/B4-08	A5/B5-08
2.1 High-temperature deposits Ring sticking Oil thickening	CECL-088-02 (TU5JP-U) 72-hour test	Ring sticking (each part) Piston varnish (six elements, avg. of four pistons) Absolute viscosity increase at 40°C between min and max values during test Oil consumption	Merit Merit mm^2/s kg/test	≥9.0 ≥RL 216 ≤0.8 × RL 216 Report			
2.2 Low-temperature sludge	ASTM D6593-00 (Sequence VG) under protocol and requirements for API (See note 4)	Avg. engine sludge Rocker cover sludge Avg. piston skirt varnish Avg. engine varnish Comp. ring (hot stuck) Oil screen clogging	Merit Merit Merit Merit %	≥7.8 ≥8.0 ≥7.5 ≥8.9 None ≤20			
2.3 Valve train scuffling wear	CECL-038-S4(TU3M)	Cam wear, avg. Cam wear, max Pad merit (avg. of eight pads)	µm µm Merit	≤10 ≤15 ≥7.5			
2.4 Black sludge	CECL-053-95(M111)	Engine sludge, avg.	Merit	≥RL140	≥RL140 + 4σ or ≤9.0	≥RL140 + 4σ or ≤9.0	≥RL140 + 4σ or ≤9.0
2.5 Fuel economy	CECL-054-96(M111)	Fuel economy improvement vs. Reference oil RL1S1 (15W-40)	%	≥2.5	–		≥2.5

Table 17.10 (continued)

Engine tests							
				Limits			
Requirement	Test method	Properties	Unit	A1/B1-08	A3/B3-08	A3/B4-08	A5/B5-08
2.6 Medium temperature dispersivity	CEC L-093-04 (DV4TD)	Absolute viscosity increase at 100°C and 6% soot	mm^2/s	≤0.60 × RL223 result			
		Piston merit	Merit	≥(RL223–2.5 pts)			
2.7 Wear see notes (6)	CEC L-099-08 (OM646LA)	Cam wear outlet (avg. max wear eight cams)	µm	≤140		≤120	
		Cam wear inlet (avg. max wear eight cams)	µm	≤110		≤100	
		Cylinder wear (avg. four cyl)	µm	≤5.0		≤5.0	
		Bore polishing (13 mm)	%	≤3.5		≤3.0	
		Tappet wear, inlet (avg. wear eight cams)	µm	Report			
		Tappet wear, outlet (avg. wear eight cams)	µm	Report			
		Piston cleanliness, four pistons	Merits	Report			
		Engine sludge, avg.	Merits	Report			
2.8 DI Diesel piston cleanliness and ring sticking	CEC L-078-99 VW TDI	Piston cleanliness	Merit	≥RL206–4 pts		≥RL 206	
		Ring sticking (Rings 1 and 2)	ASF	≤1.2		≤1.0	
		Avg. for all eight rings					
		Max for any first ring	ASF	≤2.5		≤1.0	
		Max for any second ring	ASF	0.0			
		EOT TBN (ISO 3771)	mgKOH/g	4.0			
		EOT TAN (ASTM 2896)	mgKOH/g	Report			

Table 17.11 Different requirements for the ACEA ‘C-08’ laboratory tests compared to the ‘A/B-08’ sequences

				Limits			
Requirement	Test method	Properties	Unit	C1-08	C2-08	C3-08	C4-08
1.3 Viscosity at high-temperature and high-shear rate	CEC L-036-90 (2nd Edition) (Ravenfield)	Viscosity at 150°C and $10^6 s^{-1}$ shear rate	mPa.s	$\geq$2.9		$\geq$3.5	
1.4 Evaporative loss	CEC L-40-93 (Noack)	Maximum weight loss after 1 h at 250°C	%	$\leq$13			$\leq$11
1.5 Sulphur	ASTM D5185		% m/m	$\leq$0.2	$\leq$0.3		$\leq$0.2
1.6 Phosphorus	ASTM D2896		% m/m	$\leq$0.05	$0.07 \leq 0.09$		$\geq$0.09
1.7 Sulphated ash	ASTM D874		% m/m	$\leq$0.5	$\leq$0.8		$\leq$0.8
1.8 Chlorine	ASTM 6443		ppm m/m		Report		
1.9 TBN	ASTM 2896		mg KOH/g			$\leq$6.0	

ACEA 'C' sequence engine tests:

The requirements for 2.1–2.3 and 2.6 are the same as for the 'A/B' sequences. The differences are set out in Table 17.12.

Relative to the previous sequences, the ACEA 'C(X)-08' sequences have reduced limits in C1–C3 for the M111SL engine sludge test. The fuel economy requirement in the M111FE test for the C1 sequence is increased. Replacement of the OM441LA engine test pass limits by those for the OM646LA test engine will give enhanced protection against diesel wear.

17.3.7 The ACEA 'E' Sequence Heavy Duty Diesel Lubricant Specification System

The 2008 ACEA heavy duty diesel lubricant specification system has an E-designation of E2 through to E9, plus the year date when the test was instituted, thus E9-08 as an example. First introduced in 1996, the ACEA E(X)-(date) series of specifications were based upon the Mercedes-Benz classification system. This is a clear difference from the US API system, where current standard specifications are separated from individual OEMs. Individual US tests contributing to overall specifications can be associated with individual OEMs but not the overall specification. The major changes compared to the previous ACEA 'E' 2007 sequences are the deletion of the previous 'E2' category, being regarded as obsolete, and the introduction of the 'E9-08' category, a welcome move towards convergence of the ACEA and API sequences. Each of the following grades is required to be stable and to stay in grade. However, recommendations may differ between OEM engine manufacturers so that driver manuals and/or dealers should be consulted if in doubt. The 2008 ACEA E(X)-08 series are then:

E4 – introduced 1999 as a definition of a 'ultra high-performance diesel (UHPD)' lubricant for high-performance engines used under severe operating conditions, including long drain intervals. It therefore provides excellent control of piston cleanliness, wear, soot handling and lubricant stability. Recommended for highly rated diesel engines meeting Euro I–V emission requirements and running under very severe conditions, e.g. significantly extended oil drain intervals, according to the manufacturer's recommendations. Suitable for engines without particulate filters, for some EGR engines and some engines fitted with SCR NOx reduction systems.

E6 – as for E4 but with reduced permitted levels of sulphated ash, phosphorus and sulphur (SAPS) to prevent damage to emission control after-treatment devices. It is suitable for EGR engines, with/without particulate filters and for engines fitted with SCR NO_X reduction systems.

E6 quality is strongly recommended for engines fitted with particulate filters combined with low-sulphur diesel fuel.

E7 – a 'super high-performance diesel lubricant' which provides effective control of piston cleanliness and bore polishing, further providing excellent wear

Table 17.12 Different requirements for the ACEA ‘C-08’ engine test sequences compared to ‘A/B-08’

				Limits			
Requirement	Test method	Properties	Unit	C1-08	C2-08	C3-08	C4-08
2.4 Black sludge	CEC L-053-96 M111	Engine sludge, avg.	Merit		≥RL 140 + 4σ or ≥9.0		
2.5 Fuel economy	CEC L-054-96 M111	Fuel economy improvement vs. Reference oil RL 191(15 W-40)	%	≥3.0≥	≥2.5	≥1.0 (for XW30 grades)	
2.7 Wear	CEC L-099-08 OM646LA	Cam wear outlet, avg. wear eight cams	μ	≤120			
		Cam wear inlet, avg. wear eight cams	μ	≤100	Report	≤100	
		Cylinder wear, avg. four cylinders	μ	≤5.0			
		Bore polishing (13 mm) max value of four cylinders	%	≤3.0			
		Tappet wear inlet (avg. max wear eight cams).	μ	Report			
		Tappet wear outlet (avg. max wear eight cams)	μ	Report			
		Piston cleanliness (avg. four pistons)	Merits	Report			
		Engine sludge, avg.	Merits	Report			
2.8 DI diesel piston cleanliness and ring sticking	CEC L-078-99 VW TDI	Piston cleanliness	Merit	≥RL 206			
		Ring sticking, rings 1 and 2	ASF	≤1.0	≤1.2	≤1.0	
		Avg. of all eight rings Max for any first ring	ASF	≤1.0	≤2.5	≤1.0	
		Max for any second ring EOT TBN (ISO	ASF	0.0			
		3771) and EOT TAN (ASTM D664)	mgKOH/g	Report			

control, soot handling and lubricant stability. Recommended for highly rated diesel engines meeting Euro I–V emission requirements under severe conditions, e.g. extended oil drain intervals according to the manufacturer's recommendations. Suitable for engines without particulate filters, for most EGR engines and most engines fitted with SCR NO_x reduction systems.

E9 – a new specification introduced for 2008, based on the API CJ-4 sequence, but with additional European engine performance tests which replace some US engine designs not representative of European design practice. It is as for E6, but also suitable for engines with/without particulate filters, most EGR engines and for most engines fitted with SCR NO_x reduction systems. E9 is strongly recommended for engines fitted with particulate filters and is designed for use in combination with low-sulphur diesel fuel.

There are substantial changes in the E4, E6 and E7 engine tests for 2008 from the previous sequences, where the:

- OM602A, used to measure diesel cam wear, lubricant viscosity increase, bore polish, cylinder wear and lubricant consumption and
- OM441L, used for diesel bore polishing, piston cleanliness, boost pressure loss and lubricant consumption

are replaced by the OM646LA and OM501LA, respectively, with the important requirement that these engines are run using B05 diesel, i.e. with 5% biodiesel. This reflects the fact that EN590 diesel fuel in the EU is allowed to contain up to 5% biodiesel at present. The Cummins ISM engine replaces the Cummins M11 and the Mack T12 replaces the Mack T10. The laboratory and engine test sequences for the 'E(X)-08' sequences are set out in Table 17.13. The SAPS requirements are in subsections 1.5–1.7, the effects of soot in the lubricant on viscosity are in subsections 2.2 and 2.3, soot-induced wear specifically set out in subsection 2.5 and wear generally in subsections 2.1, 2.4 and 2.6.

Across the test spectrum different emphases are laid upon bore polish, piston cleanliness, valvetrain wear, turbocharger deposits and soot-induced wear. Various engine test combinations are used for the different E-quality levels, e.g., the Mercedes-Benz tests of long duration with varying power level cycles on a repetitive basis. The Mack T11, T12 and Cummins ISM give comparability to the API 'CJ-4' series.

The major issue for the next ACEA review, probably in 2010, is the interaction of bio-fuels with the particulate filter emission control system used by OEMs. These systems could become blocked by carbonaceous matter but a regenerative strategy is used during a period where the fuel injection timing is delayed. This gives more heat in the exhaust stream which will burn the carbon in the particulate trap. The problem with delayed injection timing is the accumulation of fuel splashed onto the bore wall which is not burned and is swept off into the sump oil. As the bio-component of biodiesel is much less volatile than the diesel component, it accumulates in the sump. Being less chemically stable, it causes lubricant degradation which is evi-

Table 17.13 ACEA ‘E(X)-08’ sequence tests

Laboratory tests

				Limits				
Requirements	Test method	Properties	Unit	E4-08	E6-08	E7-08	E9-08	
1.1 Viscosity		SAE J300 Latest active issue		No restriction except as defined by shear stability and HT/HS requirements. Manufacturers may indicate specific viscosity requirements related to ambient temperature.				
1.2 Shear stability	CEC L-014-93 Or ASTM D 6278	Viscosity after 30 cycles measured at 100°C	mm^2/s	Stay in grade				
	ASTM D 6278	Viscosity after 90 cycles measured at 100°C	mm^2/s	Stay in grade				
1.3 Viscosity high-temperature/high-shear rate	CEC L-036-90 (2nd Edition) (Ravenfield)	Viscosity at 150°C and $10^6 s^{-1}$ shear rate	mPa.s	≥ 3.5				
1.4 Evaporative loss	CEC L-040-93 Noack	Max weight loss after 1 h at 250°C	%	≤ 13				
1.5 Sulphated ash	ASTM D 874		% m/m	≤ 2.0	≤ 1.0	≤ 2.0	≤ 1.0	
1.6 Phosphorus	ASTM D5185		% m/m		≤ 0.08		≤ 0.12	
1.7 Sulphur	ASTM D5185		% m/m		≤ 0.3		≤ 0.4	
1.8 Oil elastomer compatibility	CEC L-039-96	Max variation in properties after immersion for 7 days in fresh oil without pre-ageing		Elastomer type				
				REI	RE2-99	RE3-04	RE4	AEM VAMC
		Hardness DIDC	points	–1/+5	–5/+8	–25/+1	–5/+5	As per Daimler
		Tensile Strength	%	50/+10	–15/+18	–45/+10	–	
		Elongation rupture	%	–60/+10	–35/+10	–20/+10	20/+10	
		Volume variation	%	–1/+5	–7/+5	–1/+30	–5/+5	

Table 17.13 (continued)

Laboratory tests							
				Limits			
Requirements	Test method	Properties	Unit	E4-08	E6-08	E7-08	E9-08
1.9 Foaming tendency	ASTM D 892	Tendency stability	ml	Sequence I (24°C) 10 – nil			
			ml	Sequence II (94°C) 50 – nil			Sequence II (94°C) 20 – 0
	Without option A		ml	Sequence III (24°C) 10 – nil			
1.10 High-temperature foaming tendency	ASTM D 6082	Tendency stability	ml	Sequence IV (150°C) 200-50			
1.11 Oxidation	CEC L-085-99 (PDSC)	Oxidation induction time	min	R&R	R&R	≥65	≥65
1.12 Corrosion	ASTM D 6594	Copper increase	ppm	R&R	R&R	R&R	≤20
		Lead increase	ppm	R&R	R&R	≤100	≤100
		Copper strip rating	max	R&R	R&R	R&R	3
1.13 Turbocharger performance		Should a test become available before the next document update, ACEA reserves the right to set performance limits providing adequate data are available					
1.14 TBN	ASTM D2896		mg KOH/g	≥12	≥7	≥9	≥7

Table 17.13 (continued)

Engine tests							
				Limits			
Requirements	Test method	Properties	Unit	E4-08	E4-08	E7-08	E9-08
2.1 Wear	CEC L-099-08 OM646LA	Cam wear outlet (avg. max wear eight cams)	µ	≤140		≤155	
2.2 Soot in oil	ASTM D5967 Mack T8E	Test duration 300 h Relative viscosity at 4.8% soot 1 test/2 test/3 test avg.				≤2.1/2.2/2.3	
2.3 Soot in oil	Mack T-11	Min TGA soot at 4.0 cSt (100°C)	%				3.5/3.4/3.3
		Min TGA soot at 12.0 cSt (100°C)					6.0/5.9/5.9
		Min TGA soot at 15.0 cSt (100°C)					6.7/6.6/6.5
2.4 Bore polishing	CEC	Bore polishing, avg.	%	≤1.0		≤1.0	
Piston cleanliness	L-101-08	Piston cleanliness, avg.	Merit	≥26		≤17	
	OM501LA	Oil consumption	Kg/test			≤9	
		Engine sludge, avg.	Merit			Rate and report	
2.5 Soot-induced wear	Cummins ISM	Merit	mg				≥1000
		Rocker pad avg. weight loss at 3.9% soot, 1 test/2 test/3 test avg.	mg			≤7.5/7.8/7.9	≤7.1
		Oil filter diff. presection at 150 h, 1 test/2 test/3 test avg.	kPa			≤55/67/74	≤19
		Engine sludge, 1 test/2 test/3 test avg.	Merit			≥8.1/8.0/8.0	≥8.7
		Adj.screw weight loss	mg				≤49
2.6 Wear – liner ring bearings	Mack T12	Merit				≥1000	
		Avg. liner wear	µ			≤26	≤24
		Avg. top ring weight loss	mg			≤117	≤105
		End of test lead	ppm			≤42	≤35
		Delta lead 250–300 h	ppm			≤18	≤15
		Oil consumption (Phase II)	g/h			≤95	≤85

denced as a rapid increase in lubricant viscosity after an induction period. Another effect is a decrease in deposit control with biodiesel. The alternative of exhaust fuel post-injection may be favoured by OEMs due to the fuel dilution problems associated with in-cylinder post-injection.

17.4 The International Scene – ISO, ILSAC and Other Countries

17.4.1 The International Organization for Standardization (ISO)

The ISO classification for hydraulic oil viscosity is equally recognised as SAE viscosity classifications for engine and gear lubricants. An ISO working group developed worldwide performance standards and some initial proposals close to the API ‘S’ and ‘C’ series classifications were concerned with equipment and use. ISO works by consensus, and thus very slowly, implying that it will follow, rather than lead, regional developments and will therefore will always out of date most of the time. But this occurred at a time when the automotive industry required much faster response times from technical bodies to changing needs, driven by production economics. This is probably not the best route for the development of engine lubricant performance standards.

17.4.2 ILSAC – International Lubricant Standardization and Approval Committee

Concerns for lubrication classifications changing to keep up with OEM developments have been described in previous sections. A major development was the International Lubricant Standardization and Approval Committee (ILSAC), led originally by MVMA and the Japanese JAMA but increasingly international through inclusion of the Alliance of Automobile Manufacturers, AAM, and the Engine Manufacturers Association, EMA. Its view was that vehicle design had become international with trade barriers removed or reduced, therefore, lubricant specifications should be realistic and achievable worldwide. It has approved a minimum performance standard for petrol-fuelled light vehicle engine lubricants, the GF-series, as a rolling programme. GF-1 was based on API SG but additionally included an energy-conserving requirement effectively limiting the specification to low viscosity SAE 0W, 5W and 10W multigrade oils, together with other additional requirements. This restricted the marketing of GF-1 standard lubricants in Europe because viscometric requirement associated with energy saving conflicted with certain CCMC specifications. The GF-series has developed further, up to GF-4, as of 6/2004, with GF-5 specifications expected to be agreed in late 2009 with the first licences effective in mid-2010. The progress of the timeline towards this standard is given on the ILSAC web site.

GF standards set the performance requirements and chemical/physical properties of engine lubricants that OEMs require for their product's satisfactory performance and life. Responsibility for all regulatory requirements (health and safety, restrictions on use, labelling, risk minimisation to consumers and environment, etc.) remains with the lubricant manufacturer. The 'GF-' sequences are close to the API 'S' sequences but with the distinctive features of being restricted to the low viscosity 0 W/XX, 5 W/XX and 10 W/XX grades and also the energy conservation requirement in subsection 2.6 of Table 17.14. An analogous heavy duty diesel engine specification, HDH-1, has been proposed but has not obtained the widespread currency of the GF-series.

17.4.3 Japan

Japanese automotive companies used API classification systems for 'service-fill lubricants' for light vehicles. An interesting parallel with European CEC practice is that JASO, the Japanese Automobile Standards Organization, sets engine lubricant test procedures without pass/fail limits but modified its previous policy and quoted limits for a Japanese standard, JIS K2215, which specifies minimum quality engine lubricants for their gasoline engines. However, the Japanese automotive industry often does not require these tests for their own in-house specifications. Japanese engines tests are unofficially aligned with the API 'SX' sequences and are used to evaluate oils of different quality levels.

Japanese OEMs developed proprietary factory-fill specifications and then selected lubricant companies to develop those lubricants using proprietary engine tests. OEMs market these lubricants, mainly SAE 10W-30, as 'genuine oils' with about 30/35% of their market. Manufacturers are slow to reformulate these lubricants unless engines change with very few formulations changes accepted without extensive testing.

Increasing globalisation is reflected by the Japan Automobile Manufacturers Association (JAMA) working with the (US) Motor Vehicle Manufacturers Association, (MVMA), to establish the ILSAC performance standard, as in the previous subsection, containing at least one Japanese engine lubricant test. Japanese OEM diesel specifications have been slow to develop apart from a light diesel engine oil specification. On the other hand, introduction of the JASO 2T Engine Oil Standards is a prototype for the Japanese automotive industry. The main area of need is the Japanese OEMs domination of the rapidly growing Asian automotive markets.

17.4.4 Other Countries

The former Eastern Bloc (Eastern European) area, Middle East and North Africa developed separate test procedures with locally manufactured engines, intending to give performance levels comparable to API/UK military designations, the quality descriptors used for lubricants in these areas. The distinctive point was usually

Table 17.14 The ILSAC GF-4 requirements, 06/2004

Laboratory test requirements			
l.1 SAE J300	Oils shall meet all of the requirements of SAE J300. Viscosity grades are limited to SAE OW, 5 W and l0W multigrade oils.		
1.2 Gelation index	ASTM D 5133	.	12 maximum to be evaluated from –5°C to the temperature at which 40,000 cP is attained or –40°C, or 2°C below the appropriate MRV TP-1 temperature (defined by SAE J300), whichever occurs first
1.3 Catalyst compatibility	ASTM D 4951 Phosphorus,	% m/m	0.06% (mass) min, 0.08% (mass) max
	ASTM D 4951 or D 2622, Sulphur	% m/m	0.5% (mass) max, SAE 0 W and 5 W multigrades 0.7% (mass) max, SAE l0W multigrades
1.4 Volatility evaporation	ASTM D 5800 Loss at 250°C, maximum 1 h	%	15% (Note: Calculated conversions specified in D 5800 are allowed)
	ASTM D 6417 simulated distillation,	%	10% max at 371°C
1.5 High-temperature deposits	TEOST-MHT Deposit weight	Mg	35 max
1.6 Filterability	EOWTT, ASTM D 6794	with 0.6% H_20	50% flow reduction
		with 1.0% H_20	50% flow reduction
		with 2.0% H_20	50% flow reduction
		with 3.0% H_20	50% flow reduction
	EOFT, ASTM D 6795		Test formulation with highest additive (DI/VI) concentration. Read across results to all other base oil/viscosity grade formulations using the same or lower concentration of the identical additive (DI/VI) combination. Each different DI/VI combination must be tested. 50% flow reduction

Table 17.14 (continued)

Laboratory test requirements				
1.7 Foaming characteristics	ASTM D 892 (Option A)		Tendency	Stability (After 10 min settling period)
		Sequence I	10 ml max	0 ml max
		Sequence II	50 ml max	0 ml max
		Sequence III	10 ml max	0 ml max
1.8 High- temperature foaming characteristics	ASTM D 6082 (Option A)		Tendency	Stability (After 1 min settling period)
			100 ml max	0 ml max
1.9 Shear stability	Sequence VIII, ASTM D 6709	10 h stripped KV at 100°C	Kinematic viscosity must remain in original SAE viscosity grade	
1.10 Homogeneity and miscibility	Shall remain homogenous and when mixed with ASTM reference oils shall remain miscible			
1.11 Engine rusting, ball rust test	ASTM D 6557	Avg. grey value	100 min	
Engine test requirements				
2.1 Wear and oil thickening	ASTM Sequence IIIG Test	Kinematic viscosity increase at 40°C, %	150 max	
		average weighted piston deposits, merits	3.5 min	
		hot stuck rings	None	
		average cam plus lifter wear, µm	60 max	
2.2 Aged oil low-temperature viscosity	ASTM Sequence IIIGA Test	Evaluate the EOT oil from the ASTM Sequence IIIGA test with ASTM D 4684 (MRV TP-1)	The D 4684 viscosity of the EOT sample must meet the requirements of the original grade or the next higher grade	

Table 17.14 (continued)

Engine test requirements			
2.3 Wear, sludge and varnish test	Sequence VG, ASTM D 6593	Average engine sludge, merits Average	7.8 min
		rocker cover sludge, merits	8.0 min
		Average engine varnish, merits	8.9 min
		Average piston skirt varnish, merits	7.5 min
		Oil screen sludge, % area	20 max
		Oil screen debris, % area	Rate and report
		Hot stuck compression rings	None
		Cold stuck rings	Rate and report
		Oil ring clogging, % area	Rate and report
		Follower pin wear, cyl #8, average, µm	Rate and report*
		Ring gap increase, cyl #1 and #8, average, µm	Rate and report*
2.4 Valvetrain wear	Sequence IVA, ASTM D 6891	Average cam wear (7 position average) µm	90 max
2.5 Bearing corrosion	Sequence VIII, ASTM D 6709	Bearing weight loss, mg	26 max
2.6 Fuel efficiency	Sequence VIB**. ASTM D 6837	SAE OW-20 and 5W-20 viscosity grades:	2.3% FEI min after 16 h ageing, 2.0% FEI min after 96 h ageing
		SAE OW-30 and 5W-30 viscosity grades:	1.8% FEI min after 16 h ageing 1.5% FEI min after 96 h ageing
		SAE 10W-3D and all other viscosity grades not listed above	1.1% FEI min after 16 h ageing 0.8% FEI min after 96 h ageing

*ASTM Surveillance Panel will review statistics annually.

**All FEI values determined relative to ASTM reference oil BC.

Applicable Documents: SAE Standard, Engine Oil Viscosity Classification – SAE J300, SAE Handbook; SAE Standard, Standard Reference Elastomers (SRE) for Characterizing the Effects on Vulcanized Rubbers, Proposed Draft 2003-5 – SAE J2643, SAE Handbook; ASTM Annual Book of Standards, Volume 5, Petroleum Products and Lubricants, current edition; ASTM Sequence IIIG Test Research Report; M. Batko and D.W. Florkowski, Low-Temperature Rheological Properties of Aged Crankcase Oils, SAE Paper 2000-01-2943; M. Batko and D. W. Florkowski, 'Lubricant Requirements of an Advanced Designed High Performance, Fuel Efficient Low Emissions V-C Engine,' SAE Paper 01FL-265.

one national oil company in each country, who were the principal test method developers. The overall driver for local/national/regional standard test procedures was severe shortages of western currencies for specified test engine and fuels from Europe and the United States.

But these systems did not work well. Poor or non-existent correlations resulted between API performance levels and these various national test procedures. Discussion of oil quality between these national/bloc/regional organisations and lubricant/additive companies using API systems was problematical. A major contributing factor was the lack of necessary lubricant test controls, the appreciation of those quality needs and the use of non-test standard, commercial, spare engine parts and pump fuel. This occurred in Europe post-World War II, when the local, low-cost, Petter W-1 and Petter AV-I tests were developed as alternatives to the Labeco L-38 and Caterpillar 1-A tests. The previous tests and some of their derivatives were widely used until the 1980s but the opening up of political geographical blocs has led to international standardisation.

On the one hand, the cost and practical difficulties of establishing US/European tests for individual countries/blocs were prohibitive. Equally, time required, delays and costs of running engine lubricant tests in Europe/United States is expensive of a currency in short supply. As trading barriers are being removed or reduced and business globalisation increasing, then the continued use of parallel test procedures becomes unnecessary.

17.5 Other Automotive Specifications

Motor cycle and small engine lubricants are described in Section 9.7.

17.5.1 Super Tractor Universal Oils

Super tractor universal oils (STUOs), widely used in Europe and some other areas, are the extreme of multi-purpose lubricants. They arise from tractor hydraulic oils used for various hydraulic applications of agricultural machinery with added lubricant properties. STUOs have considerable advantages in reducing the number of oils required on a farm and reduce the possibility of wrong fluids in wrong reservoirs or machinery. Bulk purchases of one oil reduce unit costs against the costs of purchasing multiple hydraulic oils and lubricants.

One disadvantage of STUO oil formulations is their lack of anti-wear property for full hypoid gear axles. Key areas lubricated in a large, multi-purpose agricultural tractor are the diesel engine, manual/automatic gearbox, power takeoff gearbox and clutch, spiral bevel gear rear axle, epicyclic hub gears in the final reduction gears, oil-immersed wet brakes and pumps/actuators in the hydraulic system.

An SAE 15W-30, API CE/SG oil can be formulated with high oxidation resistance which meets API GL-4 by using ZDDP and sulphurised additives with some friction modifiers. The formulation is balanced between the lubricant requirements and the opposite requirements of the clutches and wet brakes.

17.5.2 Marine Diesel Engines

Marine diesel engines readily divide into two categories, as described in Chapter 13, where the high(er) speed engines with rpm >300 rpm are effectively much larger versions of vehicle diesel engines. These engines use a higher quality diesel fuel with defined parameters limits, such as sulphur content, cetane values.

These are large engines and long-term testing in the API/ACEA/ILSAC conventional sense, as for the previously described, relatively small, road transport engines would be so extraordinarily expensive as to be well beyond cost-effectiveness. For these engines, the lubricant specifications are an assembly of individual standard (smaller) engine tests, as defined to be appropriate. The control of bore polish over long service lives is a major issue and addressed by the inclusion of the OM 364 LA and OM602 tests, and others. The OM tests will be replaced by the OM646LA and OM441LA tests in due course, probably without the requirement to use B05 fuel as being irrelevant to marine applications. For medium and high-speed marine engine designs, the cylinder bore, main bearing and valvetrain are lubricated by the same lubricant formulation, as for smaller engines. An important consideration is the sulphur content of the fuel, now increasingly controlled and being reduced.

For low speed (50–200 rpm) high power, marine diesel engines lubrication of the bore and the crankshaft/valvetrain bearings are separated by crosshead designs which divide the two regions of the engine. The combustion chamber and piston area are subjected to combustion products arising from marine diesel fuel, an assembly of refinery reject compounds such as vacuum residues from lubricant low-pressure distillation processes, de-asphalting process residues and excess waxes – unpleasant, dirty and ill-defined substances with low cetane values. Developments in refinery technologies can upgrade these components into higher value products, consequently the overall quality of heavy marine diesel decreases further. Cetane values are low and decreasing, causing problems with combustion deposits.

Marine diesel trunk lubricants are total loss systems because the crosshead stuffing box seals ensure that they do not mix with the sump and valvetrain lubricants. They need high levels of dispersancy, to deal with combustion deposits, and high base number levels to deal with the acidity produced from the high sulphur content of the fuel. The crankcase oils are relatively lightly treated with anti-oxidants and base number additives. The Bolnes engine, with individual cylinders capable of testing separate lubricants, has been used for lubricant development. Final formulations are refined by long-term trials lasting up to several years.

17.6 Future Developments in Lubricant Specification and Performance Testing

Several trends can be identified from the description and development of the separate API, ACEA and ILSAC specification and testing systems.

- *First*, the separate specification systems will converge, but slowly, as a response to the increasingly global nature of the automotive industry. This is already demonstrated by the cross-use of individual tests in API, ACEA and ILSAC. The rate and extent of convergence between them will depend upon acceptance of the other trend of increasing service intervals, given the different time scales for service intervals in the United States and Europe. Convergence would greatly simplify lubrication specification and performance testing globally with very considerable reductions in costs.
- *Second*, the increase in service intervals for lubricant change will continue, driven by commercial and consumer pressure. European service intervals are already at 25/35 k km, and extending, for light vehicles and at 50 k+ for heavy duty diesel vehicles. US light vehicle service intervals are around half of European intervals. Various heavy duty vehicle OEMs have set a target, but yet to be achieved, of 400 k km for freight and the equivalent for off-road vehicles. The ability of the lubricant to 'stay in grade' for longer service intervals is a key issue.
- *Third*, emission standards continue to tighten towards ever-lower values, for diesel engines there is a parabolic relationship between nitrogen oxide and particulate emissions. Whilst there can be an overall reduction for these pollutants to lower levels, the latest emission requirements can only be met by trading off one pollutant against another. The choice is between lower levels of particulate by configuring engine combustion timing which gives higher levels of nitrogen oxides from the higher flame combustion temperatures. Or the nitrogen oxide emission levels can be reduced by configuring the combustion to reduced flame temperatures but with higher particulate formation. Of the two extreme options, reduction in nitrogen oxides is preferred which, for the lubricant, means considerably enhanced soot loadings.

The most recent specifications such as API CJ require an enhanced soot handling capability for heavy duty diesel lubricants, later ACEA-E series are similar. Increased dispersancy and detergency of lubricants to deal with enhanced soot levels is required.

These three major drivers have brought together the current requirements of lubricants to 'stay in grade' for increasingly longer service intervals whilst, at the same time, successfully handling higher soot levels. These aims have been achieved under an overall global scheme of lubricant specification and testing. The next major challenge will be for lubricant performance to successfully meet the challenges posed by the use of partial or full 'bio-fuels' in engines, the composition of which has yet to be established in the medium term. Those issues will be extensive fuel dilution, viscosity changes and oxidation of the lubricant.

Acknowledgements I am indebted to many colleagues who have debated lubricant specification and performance issues with me over the years. I am particularly indebted to my many former research students, now successful in industry, for their debates, discussions, encouragement and keeping me 'up to the mark'.

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