

Chemistry and Technology of Lubricants

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Editors

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Third Edition

 Springer

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ISBN 978-1-4020-8661-8

e-ISBN 978-1-4020-8662-5

DOI 10.1023/b105569

Springer Dordrecht Heidelberg London New York

Library of Congress Control Number: 2009926950

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Printed on acid-free paper

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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, ~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.

Leonardo 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.

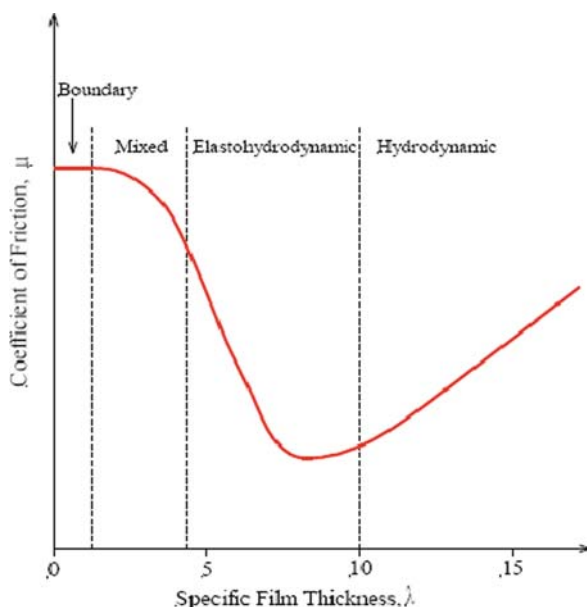
Increased power densities and throughputs placed greater attention upon the lubrication of bearings and both Tower [5] and Petrov [6] separately showed in 1883 that a shaft rotating in a lubricated bearing has a full, coherent film separating the two components. The fluid film thickness was many times 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.

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

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).

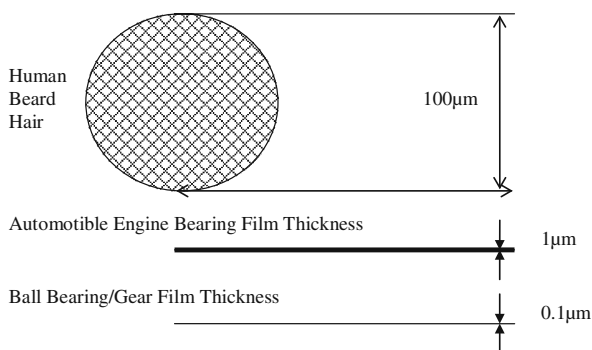


Fig. 2 Relative lubricant film thicknesses (after Dowson [12])

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 and dispersants, 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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