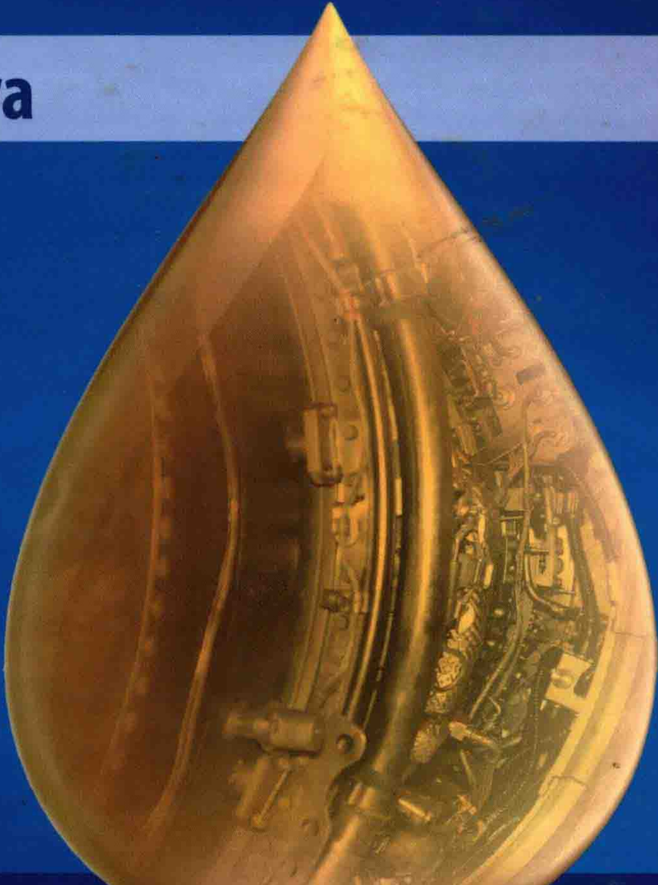
Developments in LUBRICANT TECHNOLOGY

S. P. Srivastava



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PREFACE

Lubricating oils are extremely important products without which no machinery or engines can run. Modern high-quality industrial products cannot be manufactured without the application of specific lubricants. Each class of equipment needs a distinctive product. Lubricants constitute a group of more than 600 products with different viscosity and quality levels, and hence oil companies manufacturing them continuously strive to develop and upgrade these products through extensive research and development. Lubricant development is a multidisciplinary effort that involves various fields such as chemistry, physics, metallurgy, chemical/mechanical/automobile engineering, surface science, and polymer science and requires good teamwork for successful production. There are several advanced books that deal with lubricants, lubricant additives, and tribology, but there is a shortage of a simple, concise book that would be useful for scientists and engineers who want to have in-depth knowledge on the subject. Unfortunately, this subject does not form part of a university/college curriculum, mainly because of the fact that this knowledge is regarded as a trade secret, and open literature is not available. During my 40 years of interaction with lubricant users, scientists, engineers, technical service staff, and production and marketing professionals, I have found that there is a considerable gap in knowledge between the users and developers. However, there are some organized industrial sectors, such as the OEMs, where engineers are highly knowledgeable about their equipment and lubricant requirements. If the science of lubrication and its application is understood properly by all users, tremendous benefits can be derived by realizing fuel economy, energy efficiency, reduced wear and tear of equipment, and consequently longer life.

It is with this objective that this concise book has been written, and I am confident that it would be well received by students and all those connected with the development, manufacturing, marketing, and application of lubricating oils. The book covers all the major classes of lubricants such as turbine, hydraulic, compressor, gear, transmission, gasoline engine, diesel engine, two-stroke engine, marine engine, natural gas, and rail road engine oils. However, it has not been possible to cover all the grades of minor lubricants such as specific industry-related products for the textile, cement, paper, sugar mill, and food industry. Nevertheless, it would not be difficult to understand the minor grades of lubricants after going through the major classes covered in this book.

Dr. S. P. Srivastava
Faridabad, India
June 2014

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PART I

LUBRICANT BASICS

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CHAPTER 1

INTRODUCTION: LUBRICANT SCENARIO

Lubricants are required in every machinery and engine for reducing friction, wear, and energy consumption. Depending upon the operating and design parameters of the equipment, a properly formulated lubricant can play a major role in extending equipment life and saving energy. For manufacturing modern lubricating oils, lube base oils and chemical additives are required. While base oils are produced in the refineries, chemical additives are manufactured separately in chemical plants, as it involves chemical reactions between several materials and specialized testing facilities. Currently, about 41 MMT (million metric ton) of lubricants are produced globally, and the market is growing slowly at the rate of about 2% per annum. The demand pattern has been described in several publications [1–5]. The growth is mainly in Asia. India and China are the fastest growing countries in this sector (3–5%). Asia Pacific is the largest consumer of lubricants (35%) followed by North America (28%), central and southern America (13%), western Europe (12%), and others (12%). Asian market is dominated by China (4 MMT), Japan (2.8 MMT), India (2.4 MMT), and Korea (1 MMT/year). Asia Pacific countries contribute to about 14 MMT of lubricant business per year.

These 41 MMT of lubricants constitute more than 600 grades of products to meet automotive and industrial requirements. Lubricants for automotive applications constitute the major share of lubricants (55%) followed by industrial oil (30%), process oil (10%), and marine oils (5%). Among industrial oils, turbine, hydraulic, gear, and compressor oils constitute major products (60%). About 15–20% of industrial oils are metal working oils and 5% are greases. The balance constitutes other miscellaneous industrial oils.

There are large numbers of small and major manufacturers of lubricants around the world, but in the last two decades, major consolidation has taken place, and four major global companies—Exxon-Mobil, Chevron-Texaco-Caltex, BP-Amoco-Castrol, and Total-Fina-Elf—operate. Two major regional companies—Chinese Sinopec/CNPC and India's, Indian Oil Corporation—have substantial market share in their respective countries.

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Synthetic lubricants [6] constitute about 3% of the total world lubricants. These are mainly aviation and high-temperature application fluids used in situations where mineral oil-based products cannot provide adequate service. Synthetic lubricants use several additives that are common in mineral-based products but also use special chemicals that provide high-temperature, high-pressure performance. Synthetic lubricants are based on several synthetic materials as base oils such as alkylated aromatics, polyalphaolefins, organic esters, halogenated hydrocarbons, phosphate esters, polyglycols, polyphenyl esters and ethers, silicate esters, and silicones. Synthetic oils are also used when there is a need for longer drain capabilities, lower oil consumption, fuel economy, and environmental issues like biodegradability, emissions, and recyclability. Low-viscosity multigrade engine oils like 0W-30 or 5W-30 also need synthetic base oils to meet the low-temperature viscosity requirements.

Lubricant market is dynamic, and quality levels are continuously changing. Every year, new specifications of automotive lubricants are generated to meet the OEM requirements. The use of multigrade engine oils in both gasoline and diesel engines has given a new dimension to the engine oil formulations. Multifunctional additives like dispersant viscosity modifiers change the ratio of detergent/dispersant. Use of American Petroleum Institute (API) group II, III, and IV base oils also changes the additive requirements. For example, it is possible to formulate multigrade engine oils with polyalphaolefins without or minimal use of viscosity modifiers and pour point depressants. These variations lead to the reformulation of products, and therefore, the additive pattern also changes. The demand pattern provided earlier, therefore, should serve as broad guideline only.

The last two decades have seen a very fast-track upgradation of engines, fuels, and lubricants. U.S., European, and Japanese OEM efforts have resulted in several upgraded engine oil specifications and test procedures. The highest diesel engine oil quality till 1985 was API CD level and gasoline engine oil till 1988 was API SF category. However, after 1988, there has been upgradation every year. Currently, API SN and ILSAC GF-5 for gasoline and API CJ4 for diesel engine are the latest standards for automotive lubricants. There has been a similar trend in the development of automatic transmission fluid specifications. These were, however, heavily driven by two major OEMs, General Motors and Ford, whose Dexron and Mercon fluid specifications are accepted worldwide.

This improvement in oil quality led to higher oil drain intervals, improved fuel economy, and reduced emissions. Simultaneously, the gasoline and diesel fuel quality was also improved to match the emission standards imposed by legislation. From gasoline, lead was phased out, octane number was improved, and benzene content and sulfur content were drastically reduced. Gasoline was reformulated to allow the use of oxygenates and multifunctional additives. Similarly, the diesel fuel quality was improved with respect to improved cetane number, reduced aromatics and olefin content, distillation, and drastic reduction of sulfur content. To formulate improved lubricants, it was also necessary to improve the base oil quality. API responded to this need and came out with its base oil classification, where all base oils were categorized into five groups (groups I–V). In groups II and III, sulfur levels have been reduced to less than 300 ppm and saturate content to minimum 90%. The viscosity index for group III base oil has been specified as 120 minimum. All synthetic polyalphaolefins have been categorized in group IV and remaining synthetic oil of different molecular structure in group V. To match this development in lubricant specifications, fuel quality, and base oil quality, it is obvious that the additive technology has to improve. The new specification of diesel engine oil API CJ-4 imposes restrictions on sulfur, phosphorus, and ash content, which will restrict the use of ZDDP or sulfonate/phenate detergent. Newer additives would therefore be required to formulate these and future lubricants. Biodegradability, environmental friendliness, and toxicity would further impose restrictions on the choice of additives.

Oil is limited and reserves are depleting. The search for alternate fuels is currently at its peak. Following options are currently being considered as an alternative to petroleum fuel:

1. Biofuels such as biodiesel
2. Light gaseous hydrocarbons (CH_4 based) such as CNG, LNG, coal bed methane, gas hydrate, propane, and butane (LPG)
3. Oxygen-containing fuels such as methanol, ethanol, dimethyl ether, and ethers
4. Hydrogen

The increasingly higher cost of crude petroleum and its depleting reserves is driving the development of alternate fuels. In the next few decades, we may witness a shift in the use of alternative fuels depending on the techno-commercial viability of these options. The application of CNG and biodiesel has already taken place in several countries. There is considerable activity in the development and use of biodiesel, which is nontoxic, free from aromatics, low in sulfur, and biodegradable. Biodiesel can be manufactured from renewable sources using varieties of vegetable oils and animal fats through a process of trans-esterification with methyl/ethyl alcohol. These are called fatty acid methyl esters or FAME. It may be necessary to have a separate biodiesel lubricant to take care of specific character of this fuel.

There are several technological issues, like cost of manufacture, energy requirement in the production of hydrogen, and its use in the field that needs to be addressed before hydrogen can be adopted as a transportation fuel. Hydrogen is the most ideal and clean burning fuel. With hydrogen fuel cell-based engines, the crankcase engine oils will not be required. Fuel cell-based engine will have electric motors to drive the wheels, which will require only grease for lubrication. However, hydrogen-fired engine would need special lubricant to meet the changed engine environment.

With these changes, the lubricants and their quality will undergo substantial change, and new innovative technologies need to be developed to meet the challenges lying ahead.

The book discusses various aspects of formulating modern lubricants to meet the modern industrial and automotive vehicle requirements while complying with the environmental regulations. The changes that are taking place in lubricant technology are discussed specifically.

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CHAPTER 2

CLASSIFICATION OF LUBRICANTS

Lubricants are classified in several ways; these could be liquid, semisolid (greases), and solids such as graphite, molybdenum disulfide, boron nitride, tungsten disulfide, and polytetrafluoroethylene. Majority of lubricants are, however, liquids with different viscosities and other physicochemical characteristics. Semisolid greases are used in several applications where liquid lubricants cannot be used conveniently such as in the antifriction and roller bearings of automotive/rail car wheels and other industrial machinery. Solid lubricants on the other hand are used as coatings in the fine powder form or used as additives in greases and liquid lubricants. Another classification used in the industry is based on the type of base oil utilized for the formulation of products such as the following:

1. Mineral oil-based lubricants
2. Synthetic oils
3. Biodegradable, environmentally friendly oils (based on esters or fatty oils)

Synthetic oils are based on synthetic base oils produced in a chemical or petrochemical plant such as esters, diesters, polyalphaolefins, polyalkeleneglycols, silicones, alkyl benzenes, and polyphenyl ethers. Synthetic oils are used in a wide variety of critical applications such as in engines, turbines, compressors, and hydraulic, gear, aviation, and space equipment. It is possible to formulate biodegradable oils from both selected mineral base oils and synthetic oils. However, vegetable oils and synthetic ester-based products are regarded as highly biodegradable and are preferred in those applications where spillage in soil and water is expected. These applications include products used in agricultural, forestry, outboard motors, snowmobiles, etc.

Lubricants are most conveniently classified according to their applications irrespective of the type of base oil utilized such as the following:

AUTOMOTIVE ENGINE OILS

These are further classified as gasoline engine oils, diesel engine oils, rail road oils, marine oils, two-stroke engine oils, tractor oils, off-highway equipment lubricants, gas engine oils, etc. Rail road and marine oils are also considered as a separate class

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since the chemistry used in formulating these oils is slightly different, but these are basically engine oils. The modern API classification system was established only after 1970. SAE developed viscosity classification of engine oils. Initially, three types of oils were proposed by API: regular, premium, or heavy duty. The regular type was straight mineral oils. The premium type contained antioxidants and were meant for gasoline engines. The heavy-duty oils meant for diesel engines contained both antioxidant and detergent/dispersant. This was a rough classification and did not address issues connected with the fuel differences (such as sulfur content and distillation characteristics) and operating conditions. API later developed a new system including three categories for gasoline engines (ML, MM, and MS) and three for diesel engines (DG, DM, and DS). Finally, the modern classification system was established with sequence testing, standardized testing, and performance requirements agreed by both engine manufacturers and lubricant suppliers. This practice has largely prevented the introduction of multiple OEM specifications. Presently, only Mack Truck Company's EO-X system is prevalent under the modern API licensing system. Gasoline engine oils have been classified as *SX* and diesel engine oils are given classifications in the format of *CX-2/4*. S represents service category for spark ignition engines and C represents commercial for compression ignition engines. The *X* is given in alphabetical order representing the sequence of introduction. For example, *SB* and *CB* come after *SA* and *CA*, respectively. The number 2 or 4 denotes 2T or 4T engine applications. Because of the rapid change in emission regulations and engine technology in the 1990s and onward, a new API classification comes out every 3–4 years. Before this, API-CD remained in place for a long time. The fast change presents a major challenge to the lubricant industry. Sometimes new OEM or industry specifications are reappearing faster than the API standards. For example, Cummins has issued CES 20071 1 year ahead of API-CH-4 and has again issued CES 20076 in 1999 to promote the use of premium oils with better soot-handling capability.

In Europe, engine manufacturers continue to specify their own oil requirements as of today. The specifications issued by Comite des Constructeurs d' Automobiles du Marche Commun (CCMC) have been in place for years but are now obsolete. Mercedes Benz has the most comprehensive testing and approval requirements. Volkswagen, Volvo, MAN, and others all have their own test requirements. Association des Constructeurs Europeens de l' Automobile (ACEA) has replaced CCMC in 1996, and ACEA-comprehensive specifications for gasoline and diesel engine oils applicable from the year 2012 have been issued (A1/B1-12, A3/B3-12, A3/B4-12, A5/B5-12, C1-12 to C4-12, E4-12, E6-12, E7-12, and E9-12).

INDUSTRIAL OILS

Industrial oils constitute large number of products used in a variety of industrial machinery such as in turbine, hydraulic systems, compressor, gear boxes, bearings, refrigeration, machine tools, and other industrial equipment. These are known by their names such as turbine oil, compressor oil, and gear oils.

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