ExxonMobil

Lubrication Fundamentals

Third Edition, Revised and Expanded

Don M. Pirro | Martin Webster | Ekkehard Daschner

CRC Press
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Preface

Lubrication and the knowledge of lubricants are not only subjects of interest to all of us, but they are also critical to the cost-effective operation and reliability of machinery that is, directly or indirectly, part of our daily lives. Our world, and exploration of regions beyond our world, depend on mechanical devices that require lubricating films. Whether in our homes or at work, whether knowingly or unknowingly, we all need lubricants and some knowledge of lubrication. Home appliances, lawnmowers, bicycles, and fishing reels are a small sampling of devices that have moving parts that require lubrication. The millions of automobiles, trucks, buses, motorcycles, airplanes, ships, and trains depend on lubrication for operation, and it must be effective lubrication for dependability and safety, and to reduce the environmental impact.

Many changes in the field of lubrication have occurred since the second edition of *Lubrication Fundamentals* was published in 2001. Today, intricate and complex machines are used to make paper products; huge rolling mills turn out metal ingots, bars, and sheets; metalworking machines produce very high precision parts; and special machinery is used to manufacture cement, rubber, and plastic products. Emission regulations have had a major impact on all transportation and power generating equipment and the lubricants that protect them. The use of computers, robotics, and higher technology has led to advanced machine designs that result in faster machine speeds, greater load-carrying capability, more compact equipment, smaller capacity lubricant reservoirs, higher machine temperatures, various material compatibility challenges for lubricants, restrictions in lubricant additive content, and less frequent lubrication application up to and including fill-for-life lubrication. As a result, there continues to be an explosion in higher performance and specialty application oils and greases. The impact of these lubricants on our natural environment is also a driver for new lubricant technology.

The third edition of *Lubrication Fundamentals* builds on the machinery basics discussed in the first two editions, much of which is still very applicable today. The third edition also addresses many of the new applications, and new lubricant and base stock technologies that were introduced or improved upon in the past 15 years to meet the needs of modern machinery and sustainability. The lubricants industry will continue to be faced with many challenges going forward, and innovative technologies will be needed to meet these challenges. Critical activities along the lubricant value chain that are impacted by technology include new lubrication requirements, crude oil composition and selection, base stock manufacture, product formulation and evaluation, lube oil blend plant capabilities, lubricant application, and environmental stewardship. These will be exciting times for industry, especially those participating in the quest to develop the new lubricant molecule for the future.

Don M. Pirro
Martin Webster
Ekkehard Daschner

Acknowledgments

Lubrication Fundamentals, Third Edition Revised and Expanded, like many technical publications of this magnitude, is not the work of one or two people. It is the combined work of hundreds of engineers, chemists, scientists, physicists, technologists, designers, writers, and artists—a compendium of a broad spectrum of skills and talent over a long period. The study of lubrication fundamentals starts with the scientists who research the interaction of oil films with moving components under various stresses and loads. It then takes the unique cooperation that exists between the machine designer and equipment builders, on one side, and the lubricant formulators and suppliers on the other. Additionally, collaboration often takes place with many industry associations such as the International Organization for Standardization, American Society for Testing and Materials, American Petroleum Institute, Association des Constructeurs Européens d'Automobiles, Society of Automotive Engineers, Society of Tribologists and Lubrication Engineers, Deutsches Institut für Normung, National Lubricating Grease Institute, and American Gear Manufacturers Association. This frequently culminates in the mating of the right lubricant properly applied to meet the requirements of the most efficient and demanding machines operating today.

The lubricants industry is most grateful to lubrication pioneers such as J. George Wills, the author of the first edition who identified the need for a practical resource on lubrication. He developed a vision, secured the support and resources to undertake such a monumental task, and then dedicated the effort to turn his vision into reality. We are also most appreciative for the efforts of A.A. (Al) Wessol, who was the coauthor of the second edition. Al was a true lubrication expert in many applications and was willing to share his knowledge and years of practical experience. We are privileged to be able to build on their efforts and share the many technological advances in industry.

It would be impossible to list the host of people who have helped to put this third edition together. The book compiles the many technical publications of ExxonMobil and the cooperative offerings of the foremost international equipment builders and associations. We are most appreciative to the many original equipment manufacturers and industry associations, with whom we have worked over many years, for sharing their knowledge and technology.

We thank the following senior managers at ExxonMobil Research and Engineering for their acceptance, support, and encouragement for this project: Grant Karsner, Michele Touvelle, Nick Hilder, and Bill Buck. Additionally, we recognize Jane Walter of ExxonMobil for her assistance with the book cover design and graphics.

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Ekkehard Daschner is the Industrial Lubricant Section Head and Greases Technology Program Lead at ExxonMobil Research and Engineering, Paulsboro, New Jersey. Daschner earned his mechanical engineering degree in Germany and started his career in an aluminum company. In 1982, he joined the Mobil Oil AG R&D laboratory in Germany supporting product development projects. After holding various positions in technical support, he was appointed Area Sales Director and Brand Manager in Germany and the European headquarters in London and Brussels, and later served as European and later as Global Industrial and Marine Equipment Builder Services Manager. He is recognized as an expert in lubricant applications and in particular in bearings and gearboxes.

Martin Webster is a senior research associate at ExxonMobil Research and Engineering, Annandale, New Jersey. He earned his BS and MS in aeronautical engineering and his PhD in tribology from Imperial College, London, UK. In 1986, he was awarded the Bronze Medal in tribology from the Institute of Mechanical Engineers in the UK. After spending 4 years working in the UK, he joined ExxonMobil in 1989. At ExxonMobil, Martin has held various positions in research and product development and is currently involved in the study of fundamental lubrication mechanisms at the company's Corporate Strategic Research Laboratory. His publications include peer-reviewed papers, book chapters, and patents in elastohydrodynamic lubrication (EHL), rolling contact fatigue, hydrodynamics, contact mechanics, and wear. His industry activities have included membership in the American Society of Mechanical Engineers (ASME) bearings committee and the American Gear Manufacturers Association (AGMA) gear rating committee. He has been a member of the STLE since 1989. In 2006, he was elected a director of the STLE and in 2012 he joined the executive committee. He is currently serving a 1-year term as the STLE president in 2015–2016.

ExxonMobil Contributors to the Third Edition

We would like to acknowledge contributions to the third edition from the following ExxonMobil engineers, chemists, lubricant formulators, tribologists, scientists, and technologists. Collectively, these people represent over 600 years of lubrication experience. They are not only leading experts within ExxonMobil, but many of them are recognized as among the best lubrication experts in industry:

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1 Introduction

Petroleum is one of the naturally occurring hydrocarbons that frequently include natural gas, natural bitumen, and natural wax. The name "petroleum" is derived from the Latin *petra* (rock) and *oleum* (oil). According to the most generally accepted theory today, petroleum was formed by the decomposition of organic refuse, aided by high temperatures and pressures, over a vast period of geologic time.

I. PREMODERN HISTORY OF PETROLEUM

Although petroleum occurs, as its name indicates, among rocks in the earth, it sometimes seeps to the surface through fissures or is exposed by erosion. The existence of petroleum was known to primitive man, as surface seepage, often sticky and thick, was obvious to anyone passing by. Prehistoric animals were sometimes mired in it, but few human bones have been recovered from these tar pits. Early man evidently knew enough about the danger of surface seepage to avoid it.

The first actual use of petroleum seems to have been in Egypt, which imported bitumen, probably from Greece, for use in embalming. The Egyptians believed that the spirit remained immortal if the body was preserved.

Around the year 450 B.C., Herodotus, widely referred to as the father of history, described the pits of Kir A'b near Susa in present-day Iraq as follows:

> At Ardericca is a well which produces three different substances, for asphalt, salt and oil are drawn up from it in the following manner. It is pumped up by means of a swipe; and, instead of a bucket, half a wine skin is attached to it. Having dipped down with this, a man draws it up and then pours the contents into a reservoir, and being poured from this into another, it assumes these different forms: the asphalt and salt immediately become solid, and the liquid oil is collected. The Persians call it Phadinance; it is black and emits a strong odor.

Pliny, the historian, and Dioscorides Pedanius, the Greek botanist, both mention "Sicilian oil," from the island of Sicily, which was burned for illumination as early as the beginning of the Christian Era.

The Scriptures contain many references to petroleum, in addition to the well-known story of Moses, who was set afloat on the river as an infant in a little boat of reeds waterproofed with pitch, and was found by Pharaoh's daughter. Some of these references include the following:

> Make thee an ark of gopher wood; rooms shalt thou make in the ark, and shalt pitch it within and without with pitch. (Genesis VI.14)
>
> And they had brick for stone, and slime (bitumen) had they for mortar. (Building the Tower of Babel, Genesis XI.3)
>
> And the Vale of Siddim was full of slime (bitumen) pits; and the kings of Sodom and Gomorrah fled, and fell there…. (Genesis XIV.10)

Other references are found in Strabo, Josephus, Diodorus Siculus, and Plutarch, and since then there is substantial evidence that petroleum was known in almost every part of the world.

Marco Polo, the Venetian traveler and merchant, visited the lands of the Caspian in the thirteenth century. In an account of this visit, he stated:

> To the north lies Zorzania, near the confines of which there is a fountain of oil which discharges so great a quantity as to furnish loading for many camels. The use made of it is not for the purpose of food, but

> as an unguent for the cure of cutaneous distempers in men and cattle, as well as other complaints; and it is also good for burning. In the neighboring country, no other is used in their lamps, and people come from distant parts to procure it.

Sir Walter Raleigh, while visiting the island of Trinidad off the coast of Venezuela, inspected the great deposit of bitumen there. The following is taken from *The Discoveries of Guiana* (1596):

> At this point called Tierra de Brea, or Piche, there is that abundance of stone pitch that all the ships of the world may be therewith loden from thence, and wee made triall of it in trimming our ships to be most excellent good, and melteth not with the sunne as the pitch of Norway, and therefore for ships trading the south partes very profitable.

II. PETROLEUM IN NORTH AMERICA

In the North American continent, petroleum seepages were undoubtedly known to the aborigines, but the first known record of the substance was made by the Franciscan friar, Joseph de la Roche D'Allion, who in 1629 crossed the Niagara River from Canada and visited an area later known as Cuba, New York. At this place, petroleum was collected by the Indians, who used it medicinally and to bind pigments used in body adornments.

In 1721, Charlevois, the French historian and missionary who descended the Mississippi River to its mouth, quotes a Capitan de Joncaire as follows:

> There is a fountain at the head of a branch of the Ohio River (probably the Allegheny) the waters of which like oil, has a taste of iron and serves to appease all manner of pain.

In the *Massachusetts Magazine*, Volume 1, July 1789, there is an account under the heading "American Natural Curiosities," as follows:

> In the northern parts of Pennsylvania, there is a creek called Oil Creek, which empties into the Allegheny River. It issues from a spring, on the top of which floates an oil similar to that called Barbadoes tar; and from which one man may gather several gallons in a day. The troops sent to guard the western posts halted at this spring, collected some of the oil, and bathed their joints with it. This gave them great relief from the rheumatic complaints with which they were affected. The waters, of which the troops drank freely, operated as a gentle purge.

Although the practice of deriving useful oils by the distillation of bituminous shales and various organic substances was generally known, it was not until the nineteenth century that distillation processes were widely used for a number of useful substances, including tars for waterproofing; gas for illumination; and various chemicals, pharmaceuticals, and oils.

In 1833, Dr. Benjamin Silliman contributed an article to the *American Journal of Science* that contained the following:

> The petroleum, sold in the Eastern states under the name of Seneca Oil, is a dark brown color, between that of tar and molasses, and its degree of consistency is not dissimilar, according to temperature; its odor is strong and too well known to need description. I have frequently distilled it in a glass retort, and the naphtha which collects in the receiver is of a light straw color, and much lighter, more odorous and inflammable than the petroleum; in the first distillation, a little water usually rests in the receiver, at the bottom of the naphtha; from this it is easily decanted, and a second distillation prepares it perfectly for preserving potassium and sodium, the object which led me to distil it, and these metals I have kept under it (as others have done) for years; eventually they acquire some oxygen, from or through the naphtha, and the exterior portion of the metal returns, slowly, to the condition of alkali—more rapidly if the stopper is not tight.

> The petroleum remaining from the distillation is thick like pitch; if the distillation has been pushed far, the residuum will flow only languidly in the retort, and in cold weather it becomes a soft solid, much resembling the maltha or mineral pitch.

Along the banks of the Kanawha River in West Virginia, petroleum was proving a constant source of annoyance in the brine wells; and one of these wells, in 1814, discharged petroleum at periods of from 1 to 4 days, in quantities ranging from 30 to 60 gallons at each eruption. A Pittsburgh druggist named Samuel M. Kier began bottling the petroleum from these brine wells about 1846 and selling the oil for medicinal purposes. He claimed it was remarkably effective for most ills and advertised this widely. In those days, many people believed that the worse a nostrum tasted, the more powerful it was. People died young then, and often did not know what killed them. In the light of today's knowledge, we would certainly not recommend drinking such products. Sales boomed for awhile, but in 1852, there was a falling-off in trade. Therefore, the enterprising Mr. Kier began to distill the substance for its illuminating oil content. His experiment was successful and was a forerunner, in part, of future commercial refining methods.

In 1853, a bottle of petroleum at the office of Professor Crosby of Dartmouth College was noticed by Mr. George Bissel, a good businessman. Bissel soon visited Titusville, Pennsylvania, where the oil had originated, and purchased 100 acres of land in an area known as Watsons Flats and leased a similar tract for the total sum of $5000. Bissel and an associate, J.D. Eveleth, then organized the first oil company in the United States, the Pennsylvania Rock Oil Company. The incorporation papers were filed in Albany, New York, on December 30, 1854. Bissel had pits dug in his land in the hope of obtaining commercial quantities of petroleum, but was unsuccessful with this method. A new company was formed, which was called the Pennsylvania Rock Oil Company of Connecticut, with New Haven as headquarters. The property of the New York corporation was transferred to the new company, and Bissel began again.

In 1856, Bissel read one of Samuel Kier's advertisements on which was shown a drilling rig for brine wells. Suddenly it occurred to him to have wells drilled, as was being done in some places for brine. A new company, the Seneca Oil Company, succeeded the older company, and an acquaintance of some of its partners, E.L. Drake, was selected to conduct field experiments in Titusville. Drake found that, to reach hard rock in which to try the drilling method, some unusual form of shoring was needed to prevent a cave-in. It occurred to him to drive a pipe through the loose sand and shale—a plan afterward adopted in oil well and artesian well drilling.

Drilling then began under the direction of W.A. Smith, a blacksmith and brine well driller, and went down 69 1/2 ft. On Saturday, August 27, 1859, the drill dropped into a crevice about 6 inches deep, and the tools were pulled out and set aside for the work to be resumed on Monday. However, Smith decided to visit the well that Sunday to check on it, and upon peering into the pipe saw petroleum within a few feet of the top. On the following day, the well produced the incredible quantity of 20 barrels of oil a day.

III. DEVELOPMENT OF LUBRICANTS

James Watt's development of the practical steam engine, circa 1769, introduced the industrial age. The coming of new, more demanding machines, in turn, marked the beginning of the search for improved lubricants. They were needed to meet the requirements of devices operating at constantly increasing speeds and loads. The first substances to be used were mineral oils, which were obtained from naturally occurring surface pools and extended with the addition of the already known plant and animal oils.

During the period from 1850 to 1875, many men experimented with the products of petroleum distillation then available, attempting to find uses for them, in addition to providing illumination. Some of the viscous materials were investigated as substitutes for the vegetable and animal oils previously used for lubrication, mainly those derived from olives, rape seed, whale, tallow, lard, and other fixed oils.

As early as 1400 B.C., greases, made of a combination of calcium and fats, were used to lubricate chariot wheels. Traces of this grease were found on chariots excavated from the tombs of Yuaa and Thuiu. During the third quarter of the nineteenth century, greases were made with petroleum oils combined with potassium, calcium, and sodium soaps and placed on the market in limited quantities.

Gradually, as distillation and refining processes were improved, a wider range of petroleum oils were produced to take the place of the fatty oils. These mineral oils could be controlled more accurately in manufacture and were not subject to the rapid deterioration of the fatty oils.

The latter half of the nineteenth century saw the development of many new techniques for the most efficient production of lubricants from petroleum. Not the least of these was vacuum distillation, first put to commercial use by Vacuum Oil Company of Rochester, New York, successor to Mobil Oil Corporation and present-day ExxonMobil Corporation. This process permitted the distillation of crude residuum without the use of destructively high temperatures. What set vacuum-distilled lubricants apart was reliability as machines started easier, lasted longer, and had fewer problems.

In the early 1900s, gasoline became important, and this resulted in ever-increasing demands for crude oil. Until this time, only Pennsylvania crudes were used for lubricating oil but now new processes were developed to make lube stocks from other crude sources. Some of the fatty oils continued to be used in special services as late as the early part of the twentieth century. Tallow was fairly effective in steam cylinders as a lubricant. However, it was not always pleasant to handle, because maggots developed in the tallow particularly in hot weather. Lard oil was used for cutting of metals, and castor oil was used to lubricate the aircraft engines of World War I. Even today, some fatty oils are still used as compounding in small percentages with mineral oils, but chemical additives have taken their place for the majority of users.

During the period 1910–1918, improved mechanical equipment—e.g., high-pressure steam turbines, new electrical machinery, and automobiles, placed greater demands on lubricants. Thus began the first real growth in lubricants research. This covered both refining and the new field of additive technology. It carried on, with a high level of intensity, through the 1920s and 1930s, reaching its peak during World War II. Always the impetus was the same: new innovations in machine design required new innovations in lubricant composition.

IV. HISTORY OF SYNTHETIC LUBRICANTS

A historical survey of the development of synthetic lubricants would be incomplete if it did not include mention of those oils and fats that occur in nature. In the grave of the Egyptian Tehut-Hetep (circa 1650 B.C.), there is a description of how olive oil was applied to wooden planks so that heavy stones might be moved more easily. Plinius (23–79 A.D.) compiled a list of lubricants made from plants and animals that were well known at that time and are still used today. Bearings and slow-moving machinery were lubricated from antiquity up to the beginning of the nineteenth century with oils made from olives, rape seed, castor plant seeds, and other naturally occurring friction reducers. These were the first lubricants.

The Second World War provided the primary stimulus for the development and use of synthetic lubricants. During this time, nations faced a real possibility of running short of crude oil. This challenged America's oil companies to seek ways of manufacturing lubricants and fuels from natural gas and other noncrude resources. Additionally, new devices, such as jet engines, came into being, creating new performance criteria especially in terms of high-temperature degradation resistance. Existing equipment during the war was exposed to environmental extremes—arctic and subarctic regions, for example—that led to requirements that mineral lubricants could not fulfill.

Such demands during World War II resulted in the first truly commercial use of synthetic lubricants. These are defined as products made from base fluids manufactured by chemical synthesis. Polyalkylene glycols (polyglycols) were used for lubrication in the military for the first time in 1940, although these substances had been known for about a hundred years. They were used more extensively in industry after 1945, with the end of military secrecy. Today, polyglycols are well known for use as brake fluids, high-temperature lubricants, and energy-efficient oils for gearboxes (Mobil Oil Corporation, 1999).

The chemical history of *o*-phosphoric acid esters is as old as that of polyglycols. Triphenyl phosphate was synthesized for the first time in 1854. Phosphoric acid esters attracted industrial attention for the first time around 1920 as softening agents for cellulose nitrate. In recent years, tertiary phosphoric acid esters have been further developed as defoamants, wear-resistant additives, and especially as fire-resistant hydraulic fluids.

Although research work on dibasic acid esters began long before, these materials—in their various chemical forms—assumed an important role as lubricants with the advent of World War II. On both sides of the conflict, researchers were working to develop new lubricants and fluids that would be less sensitive to temperature change—i.e., remaining more fluid at very low temperatures, and being less volatile and more stable at very high temperatures. A great deal of this effort centered on dibasic acid esters, resulting in a variety of specialty products for instruments, fire control apparatus, gyroscopes, and special aviation and naval ordnance equipment. Simple esters, although used as lubricants in early jet engines, lacked thermal stability, which limited flight time between engine overhauls to only a few hundred hours. In Germany, esters were used as automotive engine lubricants. In the early 1950s, British and U.S. researchers produced diester oils for the engines of jet aircraft, first for the military and then for commercial uses including engine oil and industrial applications. More recently, polyol esters have replaced diesters in many jet applications and specific polyol esters, which are readily biodegradable, are finding application in a wide range of equipment used in environmentally sensitive areas. Today, diester and polyol ester-based products make up the second largest synthetic market segment.

Silicone polymers were used during the Second World War in greases and instrument oils. In spite of their good physical characteristics and their high-temperature stability, they have captured only a small share of the market, largely because of their high cost. However, they are indispensable for use in certain types of precision machinery such as synchronous motors and shock absorbers, as well as very high temperature hydraulic systems. They are also used as defoamants. Other synthetic lubricants developed in more recent years include fluoride esters, polyphenyl ethers, tetraalkylsilanes, ferrocene derivatives, heterocyclenes, aromatic amines, and hexafluorobenzenes, which also have come to find use in very specialized applications.

Early work on the synthesis of hydrocarbons took place in the late 1920s and 1930s. It was based on alphaolefin technology, similar to the polyalphaolefins (PAOs) used today. These early efforts were little more than academic exercises, however, for several reasons:

1. Conventional, mineral-based lubricating oil quality was improving at a rapid rate, availability was seemingly limitless, and cost was low.
2. The raw material from which the alphaolefins were derived was in short supply.
3. Viscosity index (VI) improvers were developed, reducing the need for high VI synthetic base oils.

A fateful discovery was made by one Mobil Oil Corporation researcher on May 18, 1949. This researcher was attempting to synthesize antioxidant additive compounds by adding phosphorous or sulfur to polymerized decene alpha olefin molecules. Following good practices, the researcher included in his experiments a so-called "blank" or control sample for measuring the effects of the added elements. The experiment was a failure as it did not give the desired results, but the curiosity of the researcher persisted as the "blank" seemed like a very interesting material that looked very much like mineral oil. The new material was very unlike mineral oil in two ways. It was an excellent lubricant at high temperatures (>300°F or 150°C), and it flowed at extremely low temperatures (–70°F or –57°C). That day, the first synthetic PAO was invented, marking the second revolution in lubrication science.

Immediately after that discovery, interest in synthetics waned as petroleum supplies were cheap and plentiful with the development of the Middle East oil fields. It was not until the late 1950s that the potential of synthesized hydrocarbon PAO as a high-performance synthetic lubricant was rediscovered and a more intensive research program at Mobil Oil Corporation commenced. The real driving force for the widespread use of synthesized hydrocarbon PAOs began with the invention and successful introduction of Mobil 1™ synthetic engine oil back in 1974. What started out as an engine oil designed for high-performance vehicles and to help the United States and others conserve energy during the energy crisis of the time, Mobil 1 essentially created a "superior" category of lubricants that is still widely recognized throughout the world (Mobil Oil Corporation, 1985).

Today, synthesized hydrocarbons are used in a wide range of industrial and automotive applications and are, by far, the synthetic lubricant segment with the largest market demand. Their greatest use is for automobile engine oils. Recent advances in PAO technology have led to even greater performance attributes in the area of high and low temperature performance. Synthetic lubricants are being used in the most demanding areas of application, particularly where equipment performance and oil life is of paramount concern. In coming decades, their significance will continue to increase as equipment designs with higher operating temperatures and stresses gain an even greater share of their markets, and as their overall cost/performance attributes compared to mineral products are fully valued. Also, most importantly, synthetic lubricants will be chosen increasingly because of their ability to improve application productivity by their ability to contribute to energy conservation, extend equipment life, and reduce maintenance and downtime. Another quickly evolving area for synthetic lubricants is the development of a full range of high-performance lubricants that would be less damaging to the environment where there is potential for spills or leakage.

V. FUTURE PROSPECTS

The twenty-first century continues to see advancements in equipment technology as society places new demands on output and environmental performance. Equipment is being designed to achieve higher production levels with increased energy efficiency and lower total cost of ownership. This will result in new and different materials used in equipment, smaller equipment footprints with greater power density, advances in seal technology, finer oil filtration, smaller lubricant capacity reservoirs, higher operating speeds, increased temperatures, and higher system pressures that will all place greater demands on lubricants. These demands—coupled with the trends of reduced or maintenance-free operation, fill-for-life lubrication, the quest for more energy efficient lubricants, increased environmental awareness and regulation, sustainability, and greater attention to safety issues—will continue to challenge lubricant technology and drive associated research and development activities.

Use of alternative materials is driven by many factors such as weight reduction, increased strength, resistance to fatigue, and improvement in the surface properties that influence friction and wear. Over the past 10 years, there has been a rapid increase in the development of new wear-resistant and friction-reducing coatings. Many of these are now routinely used in commercial equipment. Because the surface now exhibits different chemical and physical properties, the interactions with the lubricant are also modified. More recently, there has been an increased focus on trying to understand how to better optimize these interactions, which may potentially lead to the development of new lubricant components and finished products aimed at taking full advantage of these new coatings. One significant challenge is the increasing number and complexity of materials used in a single piece of equipment. For example, a typical internal combustion engine contains hundreds of different interfaces that require lubrication. A new coating for a cam may not work in the piston area for which a different solution may be sought. Thus, future engines may contain a greater number of different materials for which an overall optimum lubricant needs to be found. This adds further complexity to the already challenging problem of optimizing a lubrication solution that provides an overall performance benefit across the entire engine.

The quest to develop energy sources that are more efficient and increasingly benign to the environment is already having a dramatic impact on lubrication practices and products. A recent example is the rapid growth of wind power. At first glance these systems, which are typically constructed using well-known mechanical components such as rolling element bearings, gears, and electrical generators, would appear to present no major challenges. However, what has transpired is that many of the components can suffer from a wide variety of durability issues including fretting and surface fatigue (e.g., micropitting). Traditional approaches to design, materials, finishing, and lubrication have had to be updated in order to alleviate these problems. It has also lead to the development of lubricant products specifically designed to meet the new challenges. Looking ahead, we can only imagine what new or adapted technologies will be needed to produce the energy of the future. What is known, however, is that there will be moving parts that will require lubrication.

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2 Lubricant Base Stock Production and Application

Base stock technology has undergone significant changes as refining moves through the twenty-first century. Two major factors appear to be responsible—demands for higher performance from finished lubricants and process improvements with the implementation of modern refining technology. Crude oil is still the major raw material used for manufacturing mineral oil base stocks and other associated petroleum products such as fuel, asphalt, and wax. However, new quantities of high-quality base stocks are catalytically synthesized from gaseous hydrocarbons. The gas-to-liquids (GTL) process is becoming a significant contributor to the base stock pool by converting natural gas into liquid petroleum hydrocarbons. Moreover, to satisfy lubrication performance demands under very severe operating conditions, it is necessary to replace conventional mineral base stocks with synthetic fluids such as polyalphaolefins (PAOs), alkyl aromatics, esters, polyglycols, and other special materials.

Conventional processing involving separation by distillation and solvent extraction is still widely used to produce base stocks formulated into a wide range of lubricants. As might be expected, different crude feeds and refining processes produce base oils that can vary significantly in composition and performance. It is therefore essential that crude selection and processing must be done carefully to control base stock quality. Additional processing steps, such as hydrotreating, are used to improve and maintain base stock quality. Unfortunately, even with the process step of hydrofinishing, conventional oils often fail to satisfy the performance needs when used in many modern lubricant applications. Compared to more modern conversion techniques, conventional processing yields lower quantities of comparatively low-quality base stocks. Production costs are generally higher for conventional processing, particularly for small operations without the advantage of economy of scale.

To meet many current finished lubricant performance requirements, higher quality base stocks are needed. Therefore, more severe, multiple-step catalytic processes are used. Instead of extracting existing lube molecules already present in the crude, a catalyst is used to make significant changes to the molecular structure of the crude fractions being processed. Lower value molecules are converted into more desirable lube molecules under the influence of high-pressure hydrogen and isomerization catalysts. The process is very efficient and produces high-quality base stocks at high yield off-take.

I. LUBRICANT BASE STOCKS AND THEIR APPLICATION

A. American Petroleum Institute Group I, II, III, IV, and V Base Stocks

The American Petroleum Institute (API) developed a simple classification system for lubricant base stocks as identified in API Publication 1509 Annex E. Although originally intended to help regulators interpret performance data for the licensing and certification of gasoline and diesel engine oils, the classification system is now used as a guide for base stock selection across a broad range of lubricant products. The definitions have evolved to the present five-group standard set in 1995. The API classification of these base stocks is shown in Table 2.1.

TABLE 2.1
API Base Stock Classification

	Saturates (%)		Sulfur (%)	Viscosity Index
Group I (solvent-refined)	<90	and/or	>0.03	80 to <120
Group II (hydroprocessed)	≥90	and	≤0.03	80 to <120
Group III (waxy feeds)	≥90	and	≤0.03	≥120
Group IV all polyalphaolefins (PAO)				
Group V naphthenic stocks, synthetics, and other non-PAO base stocks not in Groups I, II, III, or IV				

Groups I, II, and III are generally derived from crude, and they are most often thought of as mineral oil based.

Group IV is reserved solely for PAOs. In contrast to the separation processes used for mineral base stocks, PAOs are synthetic in origin, being built up from gaseous hydrocarbons such as ethylene.

Group V is a “catch-all” category for all base stocks not included in the first four groups. It includes both mineral-based naphthenic oils and nonconventional synthesized base stocks. Synthetic Group V base stocks are chemically created to meet severe performance requirements. Synthetic base stocks are used in significant volumes for manufacturing high-performance finished lubricants where other base stocks are likely to fail. This group includes synthetic base stocks such as organic esters, polyglycols, silicones, polybutenes, phosphate esters, and alkylated aromatics. (See Chapter 5 for more information on synthetic base stocks.)

1. Group I Base Stocks

Group I base stocks come from traditional solvent refining techniques. Group I, with higher sulfur and/or lower paraffin content, is distinctively different from mineral base stocks made by catalysis. Because solvent processing is a selective separation process, there are limits as to what can be achieved in terms of producing high viscosity index (VI) and high total saturates content. The process essentially isolates components that are present in the crude with essentially no formation of new molecules. Although crude that is considered good for lubricant base stocks may contain desirable lube molecules, these molecules are not necessarily present in significant concentrations.

Solvent refining makes use of differences in solubility to separate or remove undesirable aromatic and wax molecules from vacuum distillate lube fractions. Hydrocarbon types that are preferentially soluble in a solvent are selectively removed from the feed stream. First, to remove undesirable aromatics, polar solvents such as furfural, *n*-methyl-pyrrolidone (NMP), or phenol are used to attract and remove heavy aromatics from the vacuum distillate. Next, wax is crystallized from the feed by addition of a solvent such as ketone at refrigerated temperatures. The ketone serves as an antisolvent for the wax so it can be recovered by filtration. As a final step to making Group I base stocks, both color and stability may be improved through hydrofinishing.

Ultimately, 10–40% aromatic components remain after solvent processing. These are mostly single-ring aromatics with some sulfur-containing compounds. These components are unaffected by hydrofinishing and remain in the oil. Group I stocks generally have good solvency and natural antioxidant properties, and are desirable for better additive solubility and natural long-term oxidation control. The nature and composition of the crude oil feed can often determine the final properties of the base stock. Although Group I production is declining, there are some products where they are preferred. Moreover, there is one area where Group I has a strong presence—high viscosity base stocks that are difficult to produce by catalytic processing. Therefore, there is no anticipated end to Group I base stock production.

2. Group II and Group III Base Stocks

Group II and Group III base stocks are produced from feeds by hydroprocessing and catalytic dewaxing. Both groups share the same low sulfur and high saturates characteristics. The distinction between the two is the VI range. The VI range for Group II is the same as that for solvent processed Group I and includes base stocks with a VI between 80 and less than 120. In contrast, the minimum VI for the more severely processed Group III is 120 and above.

There are various hybrid processing routes to manufacture Group II and Group III base stocks involving combinations of both old and new technology. However, in the strict conversion process, distillate or deasphalted oil (DAO) is hydrocracked, saturating nearly all of the aromatic content of the feed. This is followed by catalytic dewaxing to convert straight-chain waxy paraffins to isoparaffins. To make Group III quality, more severe hydroprocessing is used. Alternately, GTL wax also makes good feed for catalytic isomerization to high VI base stocks. GTL base stocks are similar in composition and performance to Group III base stocks. Although synthesized from natural gas, GTL base stocks are similar to and identified as Group III base stocks.

These high-quality Group II and Group III mineral base stocks are not available in as broad a viscosity range as are conventionally refined Group I or synthetic PAOs. Commercial Group II base stocks are presently available at viscosities as high as 600 Saybolt Universal seconds (SUS) (12 cSt at 100°C), whereas Group III are limited to a maximum viscosity of 300 SUS (8 cSt at 100°C). However, with improvements in both conversion processing and GTL synthesis, it is very likely that the upper viscosity ranges of these high-quality base stocks will be extended to meet lubricant demand.

3. Group II+ and Group III+ Base Stocks

Although not officially part of the API classification, individual companies manufacture Group II+ and Group III+ stocks. These "plus" base stocks all have VIs on the high end of the API guideline. Sulfur and saturates specifications remain unchanged from the official group classification. However, individual marketers have set their own VI expectations for these unofficial grades. Among "plus" producers, the minimum VI for a Group II+ begins somewhere between 110 and 115. For Group III+, the minimum VI falls somewhere between 130 and 140. In addition to the high VI benefit, these stocks generally have lower volatility and lower pour points. The common way to reach Group III+ very high VI quality is to start by refining slack wax or GTL wax feeds.

4. Group IV Base Stocks

PAOs are paraffin-like liquid hydrocarbons with a unique combination of high-temperature viscosity retention, low volatility, very low pour point, and a high degree of oxidation resistance. The VI of these base stocks can range from 125 to more than 200 with pour points down to –85°F (–65°C). These characteristics result from the wax-free combination of relatively unbranched molecules of predetermined chain length. These properties made them ideal base stocks for high-performance lubricants. The most widely known consumer product that uses PAO base stock is Mobil 1™ synthetic motor oil.

5. Group V Base Stocks

Group V naphthenic base stocks are produced from naphthenic crude. The refining process is similar to that of their paraffinic Group I counterparts except that naphthenic crude contains essentially no paraffins, and therefore solvent dewaxing is not necessary. However, many naphthenic stocks are finished by hydrotreating. Naphthenic base stocks are characterized by having very low pour points (down to –80°F or –62°C) and low VI (typically in the range of 20–85) compared to Group I base stocks. These base stocks make them suitable for a number of specialized applications such as metalworking, process oils, refrigeration compressor oils, and automatic transmission oils.

The properties and manufacture of nonconventional synthetic Group V base stocks vary widely. These cover a broad range of materials, each having relatively unique properties that make them suitable for a number of specialized industrial, automotive, and aviation applications.

B. Base Stock Selection

Proper base stock selection is essential to the manufacture of high-quality finished lubricants. Different product lines make use of the individual performance features demonstrated by various stocks. The base stock makes up a significant portion of the finished lubricant. It contributes to finished lubricant performance features in a broad range of areas including viscosity, volatility, thermal stability, additive/contaminant solubility, oxidation stability, air release, foaming resistance, and demulsibility. The balance of lubricant formulations consists of the addition of performance-improving additives, selected according to the needs of the product being manufactured.

Formulators have a wide array of base stocks to pick from, with significant performance differences between various stocks. From a high level perspective, API base stock group classifications are used as a basis for selecting materials for lubricant manufacture. From a cost/performance assessment, the selection of the optimum base stock for a particular application is essential. With greater performance demands being made on lubricants, the need for higher quality base oils is increasing. As shown in Figure 2.1, considerable change in the marketplace is occurring as API Group II base stock is displacing Group I demand. As smaller Group I manufacturing plants are shut down, market penetration of Group II is expected to continue to dominate the demand for paraffinic base stock.

As shown in the global paraffinic base stock demand forecast, market forces are driving a slow but consistent move toward higher quality base stocks. This is primarily being led by new and changing engine oil requirements. However, marine engines and some industrial applications continue to benefit from the use of Group I base stocks, which are available in a broad range of viscosities and have greater solvency. Although many applications can use either Group I or II base stocks, Group I is in steady decline. In contrast, premium passenger vehicle and heavy-duty commercial lubricants need to use Group II/II+ and higher quality oils to satisfy industry performance requirements and meet market claims. Finally, when low temperature performance coupled with evaporative volatility control is essential, Group III+ is the one mineral oil base stock that can fulfill these performance requirements.

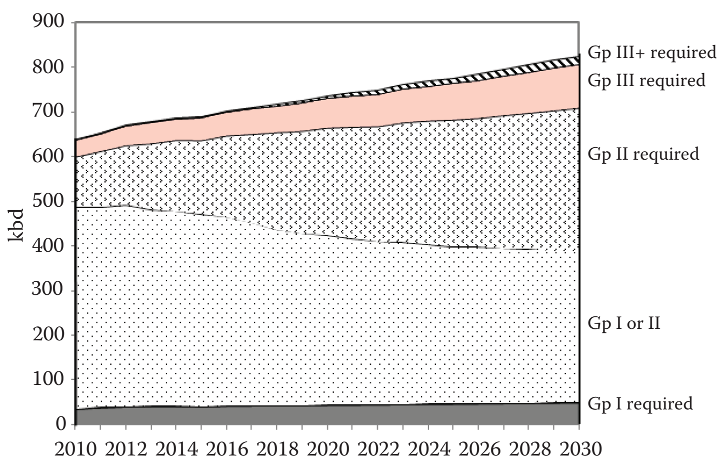


FIGURE 2.1 Global paraffinic base stock demand forecast by API classification. (From ExxonMobil assessment of publicly available information.)

Each API group has its own set of general properties that make it preferred for certain applications. Molecular composition of the hydrocarbons in base oil, along with the presence of impurities such as sulfur and aromatics, do have a significant influence on performance. As shown in Table 2.2, base stocks within a group share common characteristics. Even though base stocks may be in the same group, quality within a group can vary by individual manufacturer. As a result, it may be necessary to customize product formulations to account for those differences when changing between base oil suppliers.

Group I, also known as conventional base stock, is produced by physical extraction. Solvents are used to remove high concentrations of wax and multiring aromatic components. Group I is valued for its broad viscosity range. Unlike other mineral-based stocks, Group I is abundantly available in very high viscosities. The presence of sulfur compounds provides natural antioxidant properties. In addition, good solvency enables the oil to hold additives, keep dirt and soot in solution, and provide excellent deposit control. As Group I plants close down owing to the decline in demand, and because higher quality base stocks are available in both greater supply and at declining cost, lubricants that can be blended with Group I will continue to be reformulated and displaced with higher quality Group II or III base stocks.

Group II and III refining is typically done by hydroprocessing and catalytic dewaxing. This treatment removes impurities that affect oxidation stability. Compared to Group I, these base stocks have better thermal stability, volatility properties, and low temperature performance. Greater processing severity given to Group III produces higher VI base stocks. The higher VI is attributable to the presence of greater levels of isoparaffins. Higher quality Group II and III base stocks are necessary to meet the greater performance demands of modern engine oils.

Group III+ base stocks fill the performance gap between the best mineral-based stocks and Groups IV and V, highly synthesized stocks that are reacted to a precise chemical structure. Wax, the feed stock for manufacturing Group III+, is obtained either as a by-product from solvent refining of Group I base stocks, or it is built by linking individual molecules in the GTL manufacturing process. An isomerization catalyst is used to add branching to the molecules to produce base oil similar in quality to PAOs. Group III+ is extensively used to meet the increasingly demanding performance requirement of top-tier lubricants.

Evaporation control and good low temperature performance are important properties required to satisfy product claims. Figure 2.2 displays relative volatility and low temperature performance for typical base stocks within each API Group. The Noack test method (American Society for Testing and Materials [ASTM] D5800) measures evaporative loss of a sample subjected to heating and airflow. The Cold Crank Simulator test method (ASTM D5293) measures the apparent viscosity of engine oil, simulating the response of an average engine during a cold start. For both tests, lower results near the lower left hand corner of the graph are preferred.

TABLE 2.2
Base Stock Property Comparison

	Conventional	Hydroprocessed		PAO, Esters
Group	**I**	**II**	**III**	**IV, V**
SUS viscosity	100–2500	100–600	100–250	100–7000
Oxidation stability	Good	Good	Very good	Excellent
Volatility	Fair	Good	Very good	Excellent
Solvency	Very good	Poor/good	Poor	Poor–Excellent
Low-temperature characteristics	Fair	Good	Very good	Excellent

Note: PAO, polyalphaolefins; SUS, Saybolt Universal seconds.

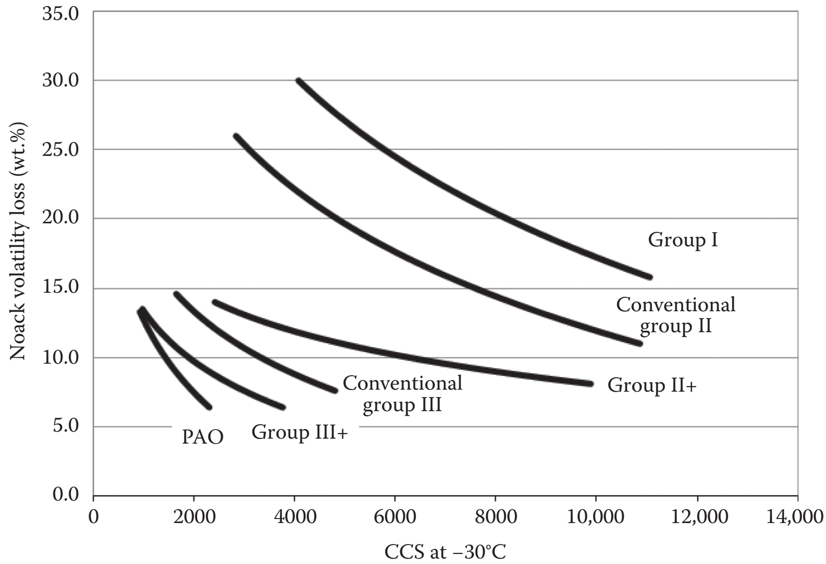


FIGURE 2.2 Blend properties of typical 4 and 6 cSt base stocks. (Note: Group II+ portrayed in the figure is optimized for both VI and volatility.)

C. Product Applications

Lube base stocks make up a significant portion of the finished lubricants, typically ranging from 70% of automotive and diesel engine oils to 99% of some industrial oils. Base stocks contribute significant performance characteristics to finished lubricants in such areas as thermal stability, viscosity, volatility, ability to dissolve both additives and contaminants (oil degradation materials, combustion by-products, etc.), low temperature fluidity, demulsibility, air release/resistance to foaming, and oxidation stability. Table 2.3 identifies whether the base stock or the additive has the

TABLE 2.3
Base Stock and Additive Impact on Lubricant Properties

Lubricant Property	Base Stock Impact	Additives Impact
Viscosity	Primary	Secondary
Viscosity stability (VI)	Primary	Secondary
Thermal stability	Primary	–
Solvency	Primary	–
Air release	Primary	–
Volatility	Primary	–
Low temperature flow	Primary	Secondary
Oxidation stability	Primary	Primary
Deposit control	Secondary	Primary
Demulsibility	Secondary	Primary
Foam prevention	Secondary	Primary
Antiwear/extreme pressure	Secondary	Primary
Color	Secondary	Secondary
Emission control	Secondary	Primary

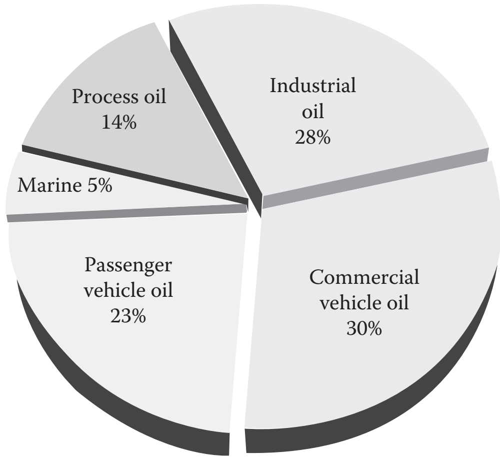


FIGURE 2.3 Estimated lubricant demand by finished product sector. (From ExxonMobil assessment of publicly available information.)

greatest influence on key properties of a lubricant. It clearly demonstrates that both the base stock and additive share responsibility for overall finished lube performance.

Modern lubricants are used in a great number of applications. No one single base stock type is able to satisfy all product requirements. An estimate of lubricant demand by the various finished product sector is shown in Figure 2.3. Demands made on the base oil vary considerably not only between but also within various sectors. For example, some heavy-duty diesel engines require some higher viscosity base stocks available only in Group I. In contrast, to satisfy low-temperature Society of Automotive Engineers (SAE) 0W passenger car engine oils, Group III or IV base stocks are preferred. Moreover, some products under severe service require Group IV or V synthetic oils to withstand extreme stresses encountered in service. Table 2.4 offers a qualitative description of the API Group classifications and their typical application.

Although often overlooked, a considerable volume of base stock is marketed as "process oil." Process oils are used throughout industry to both enhance manufacturing processes and improve "end product" performance and quality. The base stock used in a particular application is selected based on factors such as purity, solubility, viscosity, and safety. Solvent-refined materials, such as Group I base oils or Group V naphthenic base oils, are used extensively in the rubber and plastics industry to make products softer, more flexible, and easier to process. Other common uses include dust suppressants, anticaking agents, mold release oils, and carriers for ink oils, polishes, and additives. Oils refined to "white oil quality" are used where the highest purity ingredients are necessary. For example, they are used in cosmetics, food, pharmaceuticals, and lubricants that may contact food. The formulation of white oils into these products is generally covered by strict government regulations.

D. Base Oil Slate

The API base oil group classification is a part of the Engine Oil Licensing and Certification System (API Publication 1509). This is a voluntary program created by original equipment manufacturers, lube oil marketers, and base stock refiners as a guide to the selection and interchange of base stocks. The API defines a base stock slate as "A product line of base stocks that have different viscosities but are in the same base stock grouping and marketed by the same supplier." A somewhat similar system used in Europe is the Association Technique de I'Industrie Européenne des Lubrifiants (ATIEL) Code of Practice. To comply, base oil manufacturers declare that their base stocks of

TABLE 2.4
Typical Base Stock Applications by API Group

API Group	Typical Applications
Group I—Wax and multiring aromatics removed by solvent processing. Some aromatics and/or sulfur remain. Natural antioxidants, good solvency, and compatible with seals. Unlike Groups II and III, available in very high viscosities to 2500 SUS (30 cSt at 100°C) and above.	Marine and diesel engine oils, hydraulic oils, heat transfer oils, industrial gear oils, conventional greases, paper machine oils, compressor oils, machine tool way and slide lubricants.
Group II—VI performance similar to Group I except wax, aromatics, and sulfur removed catalytically. Available in viscosities up to 600 SUS (12 cSt at 100°C).	Passenger car and commercial engine oils, natural gas engine oils, automatic transmission fluid, turbine oils and automotive gear oils.
Group III—Similar to Group II but higher VI (lower viscosity change with temperature change). High severity hydro-processing eliminates ring structures beyond Group II. Has poor solvency. Viscosities up to 300 SUS (8 cSt at 100°C).	Premium passenger car motor oils (in particular, SAE 0W and 5W viscosity grades), automatic transmission fluids, food grade lubricants, white oil quality lubricants.
Group IV—Polyalphaolefins (PAO) synthetic, man-made, uniform, and free from impurities. Excellent performance at high temperature with superior oxidation stability.	High-performance engine, gear, compressor, hydraulic and circulating oils. High-performance greases, heavy duty transmissions, industrial bearing lubricants.
Group V Naphthenics—Multiring aromatics removed by solvent processing from naphthenic crude feeds. Very good low temperature performance and high solubility. Available in a wide viscosity range.	Products that operate in a narrow temperature range, at low temperatures and/or require high solubility. This includes transformer and process oils, grease, metalworking fluids, refrigeration compressor oils.
Group V Synthetics—Broad range of materials, each having relatively unique properties including alkylated aromatics, polybutenes, organic esters, polyglycols, phosphate esters, silicones.	Depending on the synthetic used: aviation turbine engines, fire-resistant hydraulic oils, heat transfer oils, brake fluids, high-temperature gear oils, refrigeration and compressor oils, chain oils and more.

Note: API, American Petroleum Institute; SAE, Society of Automotive Engineers; SUS, Saybolt Universal seconds.

different viscosities are of the same group or "slate." The intention is that, within a slate, base stocks of various viscosities must be interchangeable without affecting demonstrated performance.

For a new engine oil formulation, laboratory and engine testing to support quality claims approaching $1 million or greater may be necessary. A new formulation must pass a schedule of tests that are included in licensing guidelines. However, once a formulation is proven, there are rules that permit controlled interchange of base stocks, often with limited or no engine testing. Formulation flexibility is permitted by applying either Base Oil Interchange (BOI) or Viscosity Grade Read Across (VGRA) procedures that are part of the engine oil licensing programs. The API defines these in Publication 1509 Annex E and F. BOI defines testing necessary to make certain that performance is not affected when one base stock is substituted with another. The guidelines for both passenger car and heavy diesel engines are adjusted to be in line with current engine service categories. VGRA guidelines permit a single engine oil formulation to be converted, without further testing, to different viscosity grades after passing certification tests using the most severe grade being licensed.

Consider, for example, the EHC slate of Group II base stocks manufactured by ExxonMobil. A 10W-30 engine oil designed using EHC 50 (a branded medium viscosity base oil) must pass a rigorous testing protocol to support market claims. However, after quality claims have been demonstrated for a base oil and additive combination, BOI rules allow higher and lower viscosities of base stock within the same base oil slate to be substituted into the formula. No further engine testing is necessary for the same grade engine oil. In the BOI example demonstrated in Figure 2.4, once a single 10W-30 oil is certified, other 10W-30 engine oils may be made with the same additive formulation using a different viscosity from the EHC slate of Group II base stocks including EHC

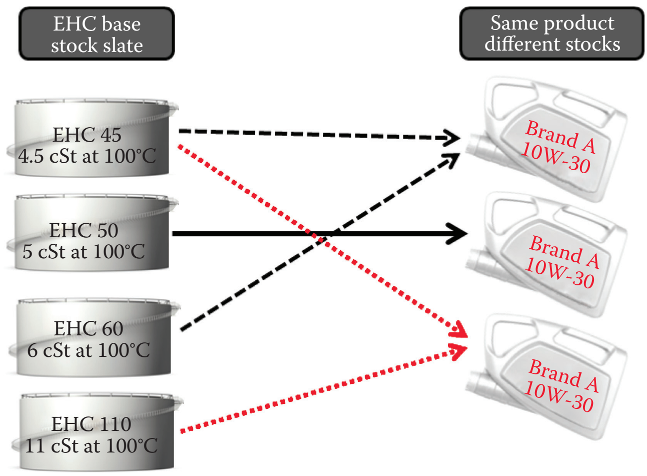


FIGURE 2.4 Example of BOI. Complete approval testing with one base stock in a slate permits blending with other base stock slate members without further certification testing to demonstrate claims.

45, EHC 50, EHC 60, EHC 110, and combinations thereof, without additional certification testing. There are many subtle variations in applying BOI, particularly when substituting one API group for another. BOI is complex and must be carefully applied even when used by a skilled practitioner.

Another practical aspect of the declaration of a base stock slate is the principle of VGRA. As illustrated in Figure 2.5, once a single grade of branded engine oil passes testing to support market claims, no further engine testing is necessary to blend a range of viscosity grades of the same brand oil. For example, the low viscosity (4.5 cSt) EHC 45 could be used to produce a branded 5W-30 engine oil. Then the 4.5, 5.0, 6.0, and 11 cSt stocks in the EHC slate could be used to blend 5W-30, 10W-30, 15W-40, and 20W-50 with essentially similar additive technology with no further engine testing. Generally, however, engine oil testing "reads across" from lighter to heavier viscosity grades.

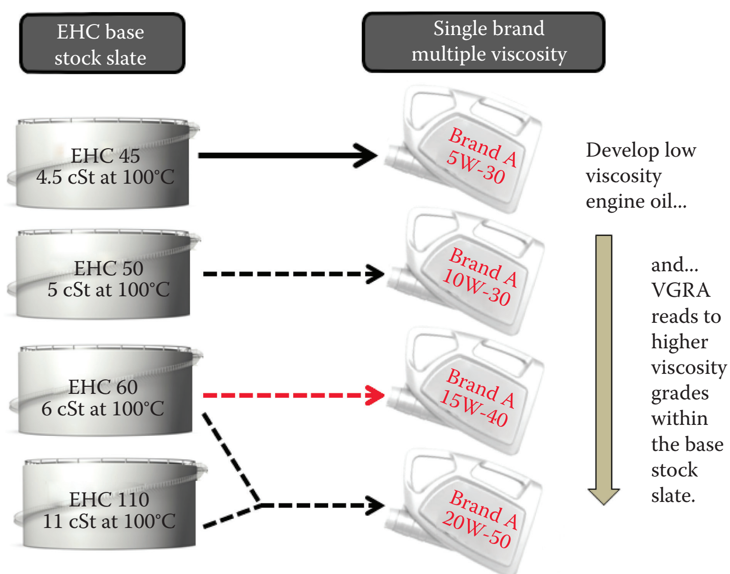


FIGURE 2.5 Viscosity Grade Read Across (VGRA). Once a single grade of branded engine oil passes testing to support market claims, no further testing is necessary to blend a range of viscosity grade oils.

A key API 1509 and ATIEL Code of Practice concept in manufacturing approvals is a declaration of the performance capability of a manufacturer's base stock slate. It is the base stock marketer's responsibility to ensure that the base oils are similar enough to enable this blending. Base stock specifications alone are not sufficient predictors of performance in finished engine oils. In general, single marketers are geographically diversifying their operations, varying refining processes, and using an increasing number of different crude feeds of varying quality. As manufacturing becomes more diverse, better control is needed to ensure consistent base stock quality. Therefore, in addition to relying on standard specifications, more attention must be given to compositional parameters, feedstock quality, and refining processes. A slate requires a single manufacturer to maintain proper control of base stock quality. BOI is best proven and backed by pertinent test data—not just "technical judgment."

II. ROLE OF CRUDE OIL IN THE MANUFACTURE OF BASE STOCK

A. Chemistry of Crude Oil

Crude oil, as it is taken from the earth, is a very complex mixture of hydrocarbons. As might be expected, the term hydrocarbon refers to the hydrogen and carbon atoms linked together and forming a majority of the individual molecules that are present. Having been transformed from living organisms being subject to heat and pressure over millions of years, the crude is termed to be an "organic" material. In addition to hydrogen and carbon, there are small amounts of other atomic elements that are present and mostly incorporated into the hydrocarbon molecules. The most common of these are nitrogen and sulfur. As part of the hydrocarbon, they are referred to as "hetero-" atoms. Heavier crude may also contain some inorganic materials such as nickel, vanadium, and iron, which are removed during refining.

Hydrocarbons form in an extraordinarily large number of configurations. They range in size from the simplest methane molecule, which contains one carbon atom and four hydrogens, to heavy asphaltic resins with structures that have not been fully mapped. Because we are dealing with mineral oil–based lubricants, we are interested in molecules of a size that fit into the range of approximately 15 to 95 carbon atoms long, corresponding roughly to a boiling range of about 300–700°C (572–1292°F). In addition, as the number of carbon atoms in a molecule increase, the number of different ways that a molecule can be structured increases dramatically. Although many different arrangements of molecules may be imagined, for practical purposes, petroleum hydrocarbons are generally classified in a limited number of ways.

Consider the list of hydrocarbon types found in crude and their associated structures as identified in Figure 2.6. The carbon atoms in each of the structures are shown as red dots. Pendent hydrogen

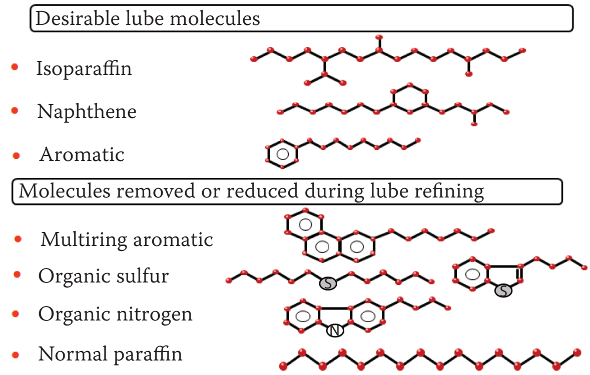


FIGURE 2.6 Typical structures of hydrocarbons found in crude.

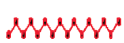
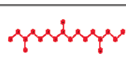
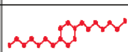
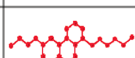
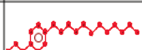
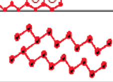
atoms are not displayed. However, each individual carbon atom has four bonds, each of which may be connected to a combination of hydrogens, a heteroatom, or another carbon. With the astronomical number of individual molecules that are possible, only a single representative structure of each is shown. Those molecules that make good lubricants are grouped at the top, whereas less desirable molecules are listed below. Nitrogen compounds promote oxidation and cause the formation of undesirable sludge. During the refining process to remove nitrogen, sulfur compounds are also eliminated. Although sulfur compounds can naturally inhibit oxidation and sludge formation, additives designed to inhibit oxidation generally provide better protection.

Characteristics that differentiate performance between hydrocarbon types are listed along the table heading in Table 2.5. Five important lubricant performance characteristics of a hydrocarbon are assessed. VI measures a lubricant's ability to resist change in fluidity with changes in temperature. Pour point is the temperature where the lubricant will begin to resist flow and cease to function as a lubricant. Oxidation resistance is essential to prevent the formation of harmful sludge and varnish. Solubility is important to not only dissolve the additives used in formulating lubricants but also to suspend contaminants that may find their way into finished oil. Finally, no assessment is complete without concern for toxicity and product safety.

There is a clear relationship between the type of hydrocarbons present in a base stock and its performance as a lubricant. As demonstrated in Table 2.5, although it is evident that some structures are better than others, no molecular type is perfect in every respect. Note that PAO, a synthetic, is included for comparison with the mineral-based materials. It is nearly perfect in every respect except solubility. However, this high-quality PAO is delivered at higher cost, which is typical for a specialty chemical.

Paraffins, having relatively simple structures, can be divided into two classes. Normal paraffins (*n*-paraffins), with simple linear structures and no side chains, turn waxy at low temperatures and make poor lubricants for products that need to operate in a wide range of temperatures. In contrast, isoparaffins, with side-branching carbon atoms to keep the molecules from crystallizing, remain fluid at low temperatures and are preferred base stock components. In addition, relative to other mineral-based materials, the isoparaffins have excellent VI, oxidation stability, and low toxicity.

TABLE 2.5
Lubricant Performance of Various Hydrocarbons Found in Crude Oil

Molecule	Structure	VI	Pour point	Oxidation	Solubility	Toxicity
n-paraffin		**Excellent**	Poor	**Excellent**	Poor	**Low**
Isoparaffin		**Good/ excellent**	**Good**	**Excellent**	**Good**	**Low**
Single-ring naphthenic		**Good**	**Good**	**Good**	**Good**	**Low**
Multiring naphthenic		Poor	**Excellent**	**Good**	**Excellent**	**Low**
Alkylbenzene		**Good**	**Excellent**	**Good**	**Excellent**	**Moderate**
Polycyclic aromatic		Poor	Poor	Very poor	**Good**	Very high
Polyalphaolefin		**Excellent**	**Excellent**	**Excellent**	**Good/** poor	**Low**

Naphthenics are similar to paraffins except that there is a grouping of carbons that form at least one ring structure generally consisting of six carbon atoms. Although the ring structure of naphthenic molecules appear similar in structure to aromatic molecules, there is one significant difference: the carbons in a naphthenic molecule are all fully saturated or filled with hydrogen. No double bonds exist between two carbon atoms in a naphthenic ring. Naphthenic molecules with one or two rings have relatively well-rounded performance. All considered, this is good, because paraffinic Group I and Group II base stocks often contain a considerable amount of naphthenic material. However, quality drops when the naphthenic content becomes too high, and/or there is a high concentration of multiring naphthenic material. With too much naphthenic material, the VI becomes too low for use in engine oils even though pour point and solubility are excellent.

Aromatic hydrocarbons are present in paraffinic lube crudes. In aromatics, the six carbon atoms in a ring share double bonds and, as a result, aromatics contain fewer hydrogen atoms than other hydrocarbons. All aromatics have poor VI properties, exhibiting significant changes in viscosity with changes in temperature. However, single-ring substituted monoaromatics are considered fair performers in conjunction with isoparaffins. They have a significant presence in the composition of lower quality Group I base stocks, and their primary contribution is to improve solubility and pour point. In contrast, polynuclear aromatics are particularly poor lubricants with respect to VI, pour point, and oxidation stability, and their highly toxic nature make them undesirable components of base stocks.

B. Crude Selection

As mentioned previously, petroleum crude is still the major raw material used for manufacturing base stocks. However, almost 90% of the crude oil that is refined ends up in nonlube products such as gasoline, distillates, and other residuum. The quality and yield of these fuels and other nonlube products can be of overriding importance in the evaluation and selection of a crude.

Historically, the preferred crude to be refined into a lube base stock is called a "paraffinic lube crude." These are sweet (low sulfur) and highly paraffinic crudes. Conventional refining involves use of various solvents to extract unwanted aromatics and separate out waxy materials. Because such processing makes no change in the structure of the crude, the desired molecules that are of lubricant quality must always be present in the crude at the start of processing. In particular, lubricant materials are contained in the atmospheric boiling range of approximately 300–700°C (572–1292°F).

Unfortunately, crude is not a uniform material, and composition can vary greatly, even between wells in the same field. Significant differences are observed from crudes around the world. Coming right from the ground, crude can range from very light condensed hydrocarbons to extremely heavy asphaltic material that needs to be heated to flow. In addition to paraffinic-based crudes, there are also those that are naphthenic in nature. Naphthenic crudes contain mostly naphthenic and aromatic components with little or no waxy paraffin. In contrast to paraffinic base stocks of the same viscosity at 100°C (212°F), naphthenic oils remain liquid at much lower temperatures.

Because of its complexity, identification of good crude for the production of base stocks requires more than a few simple tests. However, API gravity has historically been used as a key test to classify how suitable a particular crude is for manufacturing various products. The gravity of crude typically falls in a broad range, from a very light API gravity of about 50° API to a very heavy 10° API. (API gravity is an inverse scale—the higher the API gravity, the less dense the material.) Heavy asphaltic crude of 10° API is as dense as water and much heavier than a typical lube crude of about 40° API.

Good lube crude, suitable for solvent refining, is relatively light and traditionally falls in a range of 35–50° API. However, with advances in refinery technology, heavier crudes can economically produce high-quality Group II and III base stocks. For example, with hydrocracking and catalytic dewaxing along with hydrofinishing, heavy sour crude such as Hamaca from Venezuela with an API gravity of 26° API yields high-quality base stock. How far down in API gravity a refinery can go, and still make quality lubricant molecules, depends on refining capability and economics. There are practical limits to how heavy a feed can be. Heavy asphaltic crudes in the range of 10–20° API contain catalyst plugging materials that will quickly deactivate catalyst and terminate processing.

Another usual measure of crude quality is sulfur content, being labeled as sweet or sour based on its sulfur content. Sweet is considered to be less than 0.5% sulfur by mass and sour is greater than 1.0% sulfur. Anything between 0.5% and 1.0% is an "intermediate." Table 2.6 lists the properties for a few crudes from around the world. West Texas Intermediate, which is often used as a benchmark against which others are compared, is a good quality sweet lube crude. Because it is easier to make value-added products with lighter sweet crudes, they generally command a premium price over heavier sour crudes.

Identification of good lube crudes go beyond the simple measure of gravity and sulfur content. Analysis of a proposed new crude generally begins by separating it into fractions by distillation. Each fraction is then tested to determine if it has the right components to be able to turn it into a good base stock. Final confirmation on whether quality lubricants can be made from a new crude supply is done by actually putting it into a closely monitored refinery run. This is followed by testing both the base stocks and the products into which they are formulated.

A breakdown of the molecular constituents in a typical lube crude is shown in Figure 2.7. Different classes of molecules are sorted by the number of carbon atoms for the molecules present, starting with the light molecules on the left progressing to the heavier components on the right. The lightest molecules of interest for lubricants begin with a carbon number of about C17, corresponding to an atmospheric boiling point of about 300°C (572°F) (i.e., at a temperature where there are about 17 carbon atoms in each individual molecule). Identification of the constituents by chromatographic separation ends at a carbon count of about C95. This generally corresponds to the largest molecules that are present in high viscosity base stocks as well as the capability of conventional analytical separation instruments.

TABLE 2.6
Crude Oil Properties

Crude Name	°API	Crude Type	Sulfur (Mass %)	Sulfur Level
Bachaquero (Venezuela)	17	Heavy asphaltic	2.4	Sour
Alba (UK)	20	Heavy asphaltic	1.2	Sour
Maya (Mexico)	22	↑	3.4	Sour
Hamaca (Venezuela)	26		1.6	Sour
Arabian Heavy	28		2.9	Sour
Arabian Light	32		1.8	Sour
Alaskan North Slope	32		0.9	Intermediate
Brent (North Sea)	38		0.4	Sweet
Statfjord (Norway)	39	↓	0.2	Sweet
West Texas Intermediate	40	Conventional light	0.3	Sweet
Tapis (Malaysia)	46	Conventional light	0.1	Sweet
Arabian Super Light	51	Conventional light	0.1	Sweet
Condensate	65	–	–	

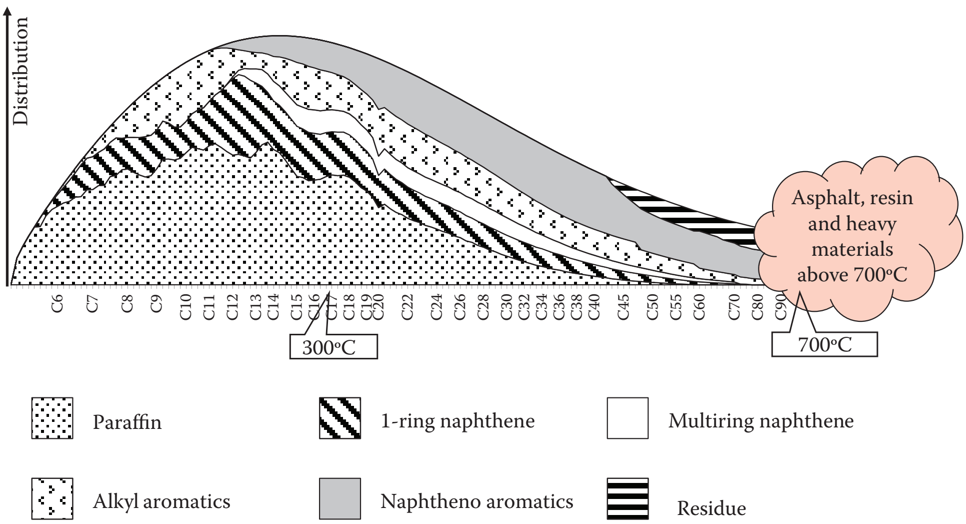


FIGURE 2.7 Hydrocarbon distribution in a typical lube crude versus carbon number.

III. REFINERY PROCESSING—SEPARATION VERSUS CONVERSION

Conventional solvent processing of crude relies on physical *separation* of the preferred lube molecules from the remaining materials in the crude. Separation in refining is often accomplished by distillation and solvent extraction. Therefore, to make Group I base stocks, lubricant quality molecules must be present in concentrations that make processing worthwhile. Aside from some hydrofinishing to remove impurities and partially saturate remaining aromatics, solvent process molecules are essentially unchanged.

Modern lubricant *conversion* technology creates lube molecules through conversion and upgrading of nonlube components in the crude. Instead of simply extracting existing molecules from the crude, it relies on high temperature and high pressure hydrogen to saturate aromatics, break apart, and rearrange common molecules into high quality lube base stocks. Therefore, conversion processing can use a much broader range of crude types than conventional solvent processing, including less expensive crudes. Ultimately, conversion processes create greater volumes of more valuable lube base stocks with less costly processing.

A description of both separation and conversion processing processes follows. There are many exceptions to these schemes. As refineries are upgraded, modern lube refining techniques have been successfully integrated into existing refinery operations. For example, solvent dewaxing can effectively be replaced by catalytic dewaxing, solvent extraction can be used to condition feed going into a conversion process, fractionation of streams can take place at various points in a process. Therefore, in the world of lube processing, hybrid systems are very common. Separate and more in-depth discussion of the separation versus conversion processes will begin following the section on vacuum distillation (Section III.B), a process common to both operations.

A. Atmospheric Distillation

Before either separation or conversion processing begins, it is necessary to clean the crude and subsequently separate off lighter components by distillation. It is necessary to remove inorganic salts, suspended material, and water. Salt and sludge can break down during processing to form acids that cause severe corrosion of refinery equipment, plug heat exchangers and process equipment, and poison-sensitive catalysts. Cleanup is accomplished by mixing the crude with additional water to dissolve salts and sediment, adding processing chemicals to speed separation, and allowing the contaminants to settle out of the crude.

Atmospheric distillation is next, as shown in Figure 2.8. The desalted crude is pumped through a furnace where it is heated and partially vaporized. The mixture of hot liquid and vapor from the furnace is put into a fractionating column called a tower. The tower operates at a pressure slightly above atmospheric and at a temperature range where the hydrocarbons will boil without cracking. The bottom of the tower operates at a higher temperature than the top. As vapor moves up the column, heavier components condense out and pass down. A multiple series of trays is stacked inside the tower to hold condensed liquid. These multiple trays ensure that as the vapor stream moves up the column, lower boiling vapors are progressively condensed and flow down the column. This fractional distillation separates the feed into multiple narrow boiling range cuts that cannot be duplicated in a simple single pot still.

Different products are drawn from the atmospheric tower at various heights along the column. Naphtha and gaseous hydrocarbons are carried over the top. The naphtha is condensed from the vapor and further processed into gasoline. Kerosene, diesel, and gas oils are withdrawn as side cuts from the successively lower and hotter levels of the tower and used for fuel. A heavy black, atmospheric residuum is collected at the bottom. Because the residuum tends to thermally decompose at about 370°C (700°F), any further distillation of the material from the tower bottoms would cause these bottoms to decompose. Further separation must be done under high vacuum where the components will boil at lower temperatures without cracking.

Boiling point distribution of light products is shown in the center row of Figure 2.9. Distribution is plotted against both atmospheric equivalent boiling point in degrees Celsius and average carbon number of the cut. Similarly, the distribution spectrum for various base stocks by viscosity class is shown in the top row of the graph. (Distillation temperatures for the base stocks have been mathematically converted to theoretical boiling points at atmospheric pressure.) Viscosity grades are given in terms of SUS. Base stock viscosity grades can be manufactured in a range varying from a very low viscosity of 70 SUS (3 cSt at 100°C) to 2500 SUS (30 cSt at 100°C) for bright stock.

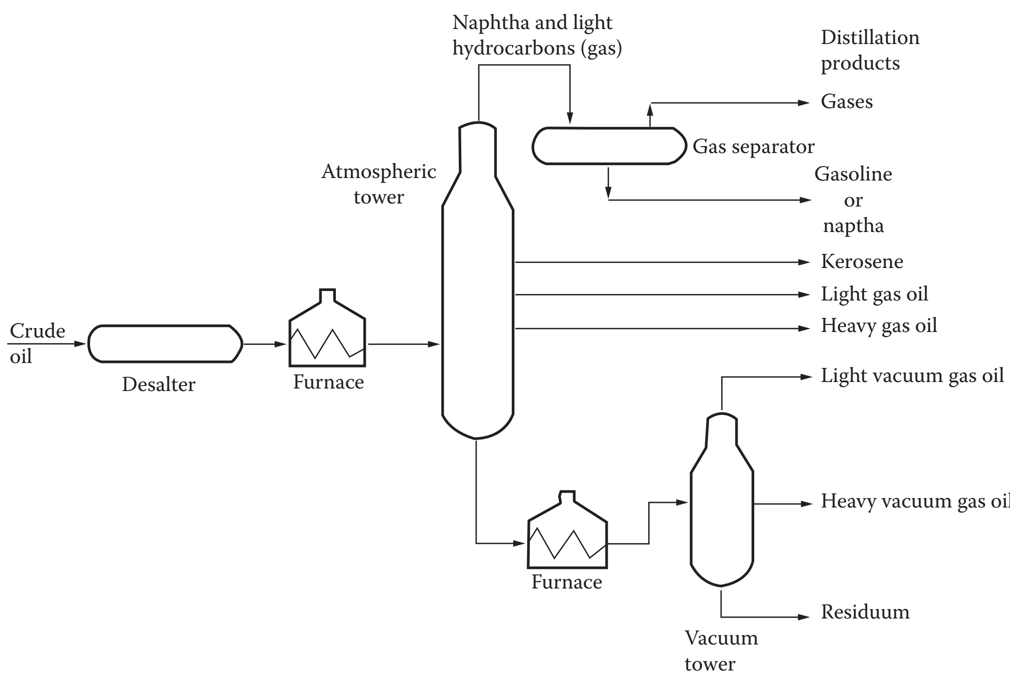


FIGURE 2.8 Crude distillation unit.

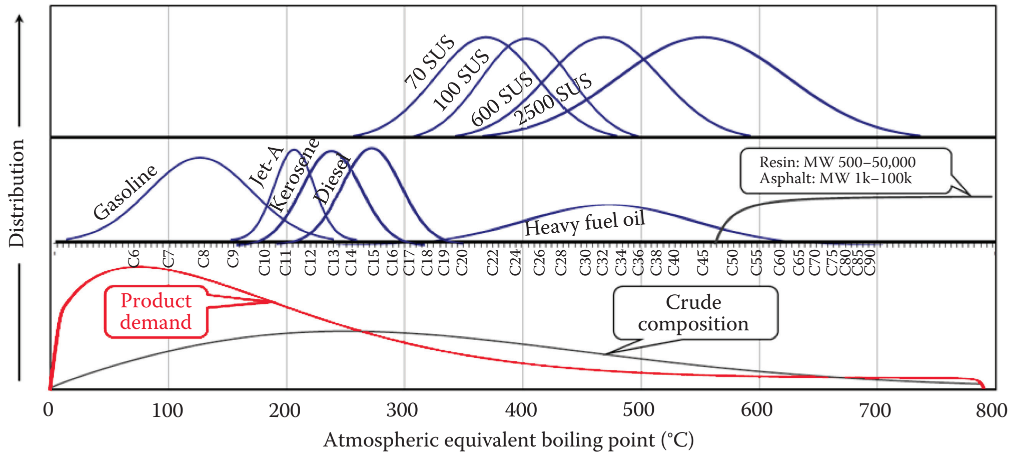


FIGURE 2.9 Products across the distribution spectrum. This graph shows the product volume distribution versus the atmospheric boiling point and the number of carbon atoms in a typical molecule. Lube fractions in the top row are identified by viscosity in SUS, which has been the traditional viscosity measurement for Group I base stocks in commercial practice.

B. Vacuum Distillation

Vacuum distillation is the first process in base stock production for both conventional solvent processing and hydrocarbon conversion processing. The heavy fraction of crude from the atmospheric tower bottoms, a mix of materials boiling above 350°C (662°F), is fed to the bottom of the vacuum tower. Lighter materials rise to the top of the tower, whereas the heavy asphalt, resins, and heavy lube stock remain at the bottom. Notice in Figure 2.9 that there is overlap between the various viscosity grades. This overlap may vary slightly according to the capability of the equipment to separate the extremely complex mixture of molecules present in the feed. Careful operation of the vacuum tower is necessary to prevent too much overlap that would cause processing problems downstream and result in inferior product quality. Base oil properties set by vacuum distillation include viscosity, flash point, and volatility.

Similar to atmospheric distillation, the vacuum tower separates the heavy fraction of the crude into different viscosity classes by boiling range. Unlike the atmospheric unit using multiple trays to effect separation, instead, packing is used to reduce the pressure drop in the vacuum tower. Packing generally consists of small ceramic, metal, or plastic shapes randomly laid down in the column. Alternately open structured monolithic packing can be fitted into the column. Packing permits contact of vapor with liquid without the restriction of having to pass through liquid-filled trays as it rises up the tower. Only a few special trays, called draw trays, are used at various points in the column to enable collection and removal of liquid at the points where product side streams are drawn.

In operation, the pressure at the top of the column is reduced to less than one-tenth of normal atmospheric pressure. The heavy crude fraction is heated in a furnace to about 400°C (752°F) and fed into a flash zone near the bottom of the column. At atmospheric pressure, the feed will not vaporize; however, separation can begin at reduced pressure under a vacuum. As the vapor rises in the column, heavier components condense on the packing and move downward. The lightest components continue to move up the column. Neutral distillate withdrawn from the side streams consists of fractionated liquid with a small amount of lower boiling material. Therefore, each side stream is charged to a stripping unit, where steam is used to strip out low boiling materials to prepare the neutral distillate for further processing. The low boiling material is charged back to the vacuum tower to provide cooling and for further fractionation.

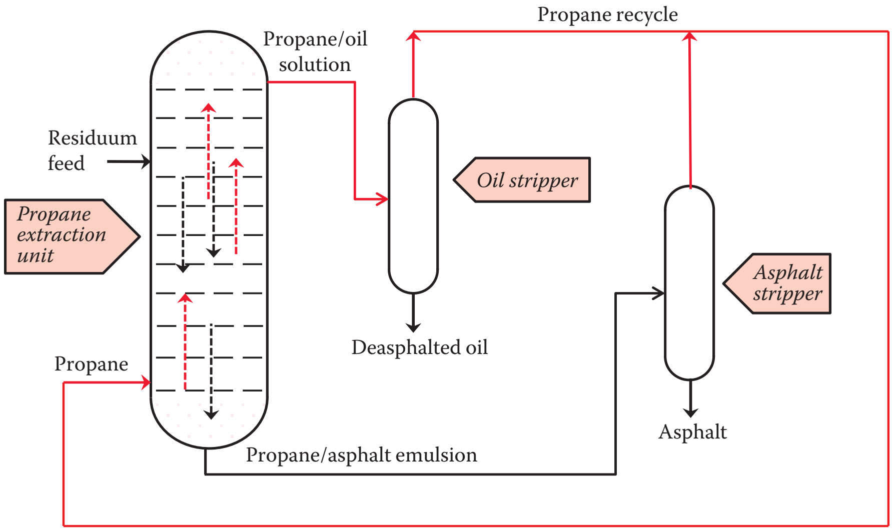


FIGURE 2.10 Continuous propane deasphalting process.

C. Propane Deasphalting

The vacuum residuum collected at the bottom of the tower is typically steam stripped in a stripping section below the flash zone before leaving the tower. The residuum contains the lube fraction in combination with a complex mixture of asphalt and resin. The extremely high viscosity, nonlube components are removed producing a DAO for further lube manufacture. Separation is typically done by extracting the lube fraction with propane solvent in a propane deasphalting unit. Propane is used as an extraction solvent because it will dissolve paraffinic, naphthenic, and aromatic lube fractions from the residuum. After the propane extract is decanted from the heavy asphalt layer, the low boiling propane solvent is evaporated leaving a DAO. Asphalt and resins are not soluble in propane and form a separate liquid phase.

In practice, deasphalting is done continuously in a countercurrent flow extraction unit as diagrammed in Figure 2.10. The residuum, usually diluted with a small amount of propane, is pumped to the middle of an extraction column full of liquid propane. At the same time, propane is injected into the bottom of the column at about 6–8 times the residuum volume. Because the residuum is denser than propane, the residuum flows down the column, with the propane rising up in a counter flow. The two streams are mixed together within the column and the lube fraction dissolves in the propane and continues up the column. The heavy, insoluble asphaltic material passes out of the bottom of the column. The propane and asphalt streams are sent to separate stripping towers, where propane is recovered and recycled. The DAO is next processed in the same manner as the other lower viscosity lube distillates.

IV. CONVENTIONAL SOLVENT PROCESSING

Conventional solvent processing (see Figure 2.11) involves separating existing lube molecules from crude where those molecules already exist. After vacuum distillation, *solvent extraction* is used to remove aromatics, particularly the polynuclear aromatics that have low VI, high pour point, and poor oxidation stability. Next, *solvent dewaxing* removes the waxy straight-chained paraffins that negatively affect pour point and cold flow properties. In the final step, *hydrofinishing* improves the color and stability of the finished Group I base stock.

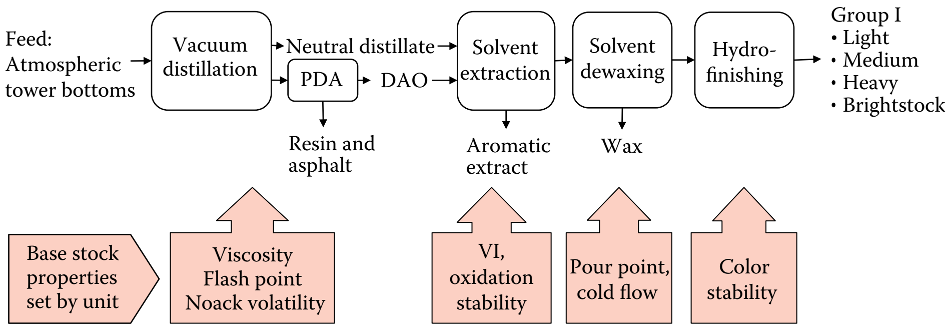


FIGURE 2.11 Conventional solvent refining process to make Group I base stocks.

A. Solvent Extraction

Solvent extraction is applied to both neutral distillates and the heavier propane DAOs. The process works by separating out the poor-quality aromatic molecules from the higher-quality lube components. Out of the extraction unit, the fraction containing desirable lube molecules is called a raffinate, and the extracted low VI phase is called the aromatic extract. For good separation, the choice of solvent is very important. A solvent should have good solvency for the aromatic fraction, while having little or no solubility for the saturated fraction. In addition, the solvent should have a higher density than the raffinate to simplify phase separation, and a relatively low boiling point to aid recovery and recycle after the raffinate and the extract exit the extractor. Several highly polar materials are used extensively as solvents in commercial production: furfural, NMP, and phenol.

In practice, separation takes place by countercurrent extraction in a vertical tower (see Figure 2.12). The various viscosity cuts from the vacuum distillation tower are processed one at a time in block mode to maintain the viscosity grades established by the vacuum tower. The distillate charge is fed into the side of the unit. The extraction solvent enters near the top and flows down the tower, dropping because of its higher density. A series of rotating-disk contactors and baffles drive intimate contact between the rising distillate feed and the descending solvent stream. Aromatics, along with some sulfur/nitrogen compounds, migrate into the solvent phase as it passes down the tower. After exiting the tower bottom, the extract mixture goes to solvent recovery. Recovered solvent is recycled back to the extractor, and the extract is generally cracked into fuel.

As the raffinate stream exits the top of the tower, it contains only a small amount of solvent that is recovered by evaporation and steam stripping. At this point, the raffinate is relatively free of

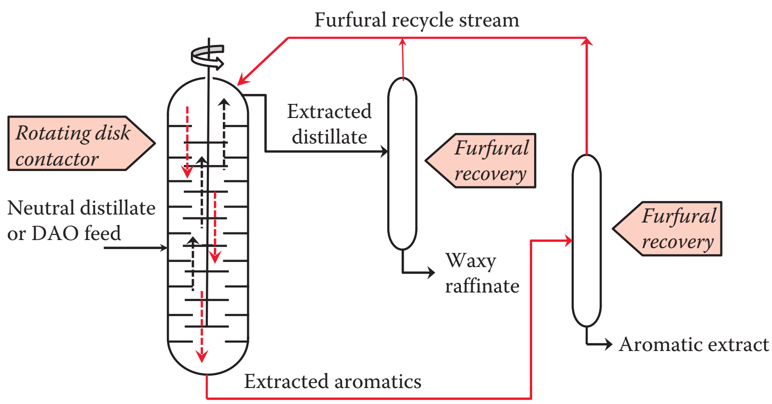


FIGURE 2.12 Counter current extraction of aromatic hydrocarbons in a rotating disk contactor using furfural as the solvent.

aromatics, particularly those with multiple rings, and is ready for solvent dewaxing. The extent of extraction is controlled by unit operating temperatures, distillate and solvent feed rates, and solvent type. The most evident effects of solvent extraction are increases in VI of the raffinate along with an approximate 50% decrease in sulfur. In addition, there is also a significant improvement in both thermal and oxidation stability. At this point, the raffinate still contains a significant amount of wax that will require removal by solvent dewaxing.

B. Solvent Dewaxing

The purpose of dewaxing is to remove normal paraffins from the waxy raffinate in order to improve its low-temperature performance properties. A mixture of solvents, methyl ethyl ketone (MEK) and toluene, cause the normal paraffins to form crystals at reduced temperatures. The wax crystals are then separated from the oil by filtration. (This is in contrast to phase separation used in the earlier solvent extraction process.) The function of the individual solvents is not entirely clear. Nevertheless, the combination of solvents does adjust the polarity of the solvent to optimize wax precipitation. Other solvent combinations such as MEK/methyl isobutyl ketone are also commonly used.

The first step in MEK dewaxing (see Figure 2.13) is to condition the feed stream by mixing it with solvent and heating it to dissolve the oil and wax. Only wax formed under carefully controlled process conditions can guarantee optimum crystal structure for filtration. After heating, a pair of double-pipe heat exchangers is used to cool the feed to a temperature that is about 5–10°C (9–18°F) below the desired pour point. As the feed passes through the central pipe of the heat exchangers, wax crystals form on the chilled wall surface. To maintain filter efficiency, a rotating blade scrapes the wax off the walls and into the process stream. Additional solvent may be added throughout the process to promote wax crystal formation in the wax slurry.

The wax slurry is collected in a surge tank before it is fed to a rotary vacuum drum filter. Separation of wax from oil takes place on a filter cloth fitted to the outside of a cylindrically framed drum. The drum is suspended on its side and rotated on its central axis through the wax slurry. As shown in the end view of a filter drum in Figure 2.14, the filter drum is segmented into separate chambers to permit variations in vacuum and pressure on the filter cloth as it cycles. A series of

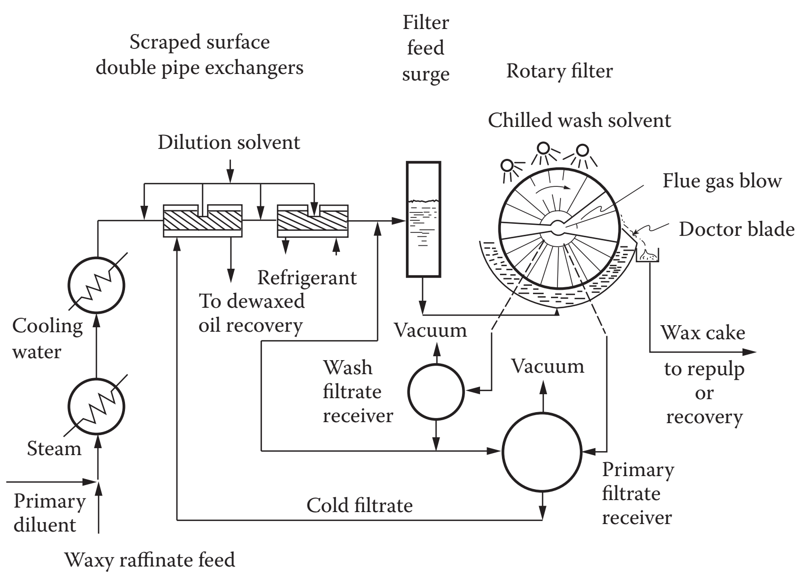


FIGURE 2.13 MEK solvent dewaxing process.

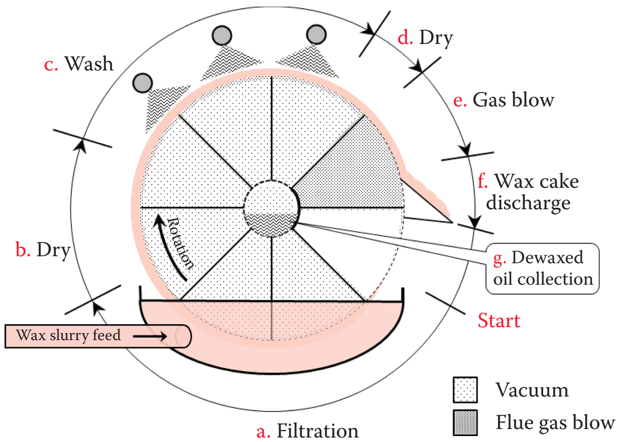


FIGURE 2.14 Wax collection cycle for a rotary drum filter.

valves, located near the central axis of the drum, channels the dewaxed oil passing through the filter to solvent reclamation.

As shown in the wax collection cycle, no vacuum is applied at the "Start" of a cycle before a filter segment passes into the slurry trough. This prevents loss of vacuum through the uncoated filter. Filtration begins (a) as a filter segment enters the wax slurry and a vacuum pulls the filtrate oil through the filter leaving the wax on the filter cloth. The wax continues to build in thickness through the filtration cycle. The vacuum continues as (b) the segment leaves the wax slurry and goes through a short period of drying to remove more oil and solvent from the wax. In the wash cycle, (c) cold solvent is sprayed on the wax to displace more oil from the cake. (d) The wash is followed by another short period of drying. Finally, (e) the vacuum is lifted from the filter with pressure from a flue gas blow and, as the filter drum rotates, (f) the wax is guided from the drum by a doctor blade and is passed by the conveyor to a wax solvent recovery system. At this point, the filter cloth is empty and the cycling continues.

The dewaxed filtrate is removed continuously (g) through a complex set of pipes and valves located in the drum and sent to solvent recovery. Solvent recovered from both the oil and wax phases is recycled back for use in the solvent dewaxing process. After the dewaxed oil is free of solvent, it is often subjected to a light hydrofinishing to improve quality.

The wax that was separated from the oil still contains a relatively high amount of oil. This oily wax is called "slack wax" and, depending on wax disposition, usually contains approximately 15–30% oil. To make a high-quality, fully refined wax, the oil content of the wax is usually reduced to less than 1% through a deoiling process. However, as an alternative to making finished wax, slack wax from conventional solvent processing of middle distillates can be catalytically converted to high-quality Group III+ base stocks. Catalytic isomerization is covered in Section V.

C. Hydrofinishing

Hydrofinishing is often done as the final step in solvent processing. In this process, hydrogen is reacted with an oil to improve base stock color by removing small amounts of sulfur, other heteroatom components, and polar contents. The hydrofinishing reactor consists of a bed of catalyst through which the hot oil contacts a relatively low-pressure hydrogen feed (200–300 psi or 1379–2068 kPa). Essentially no chemical change occurs with the higher performance lube molecules. The process has very little effect on the key physical properties represented in marketing the base stock. However, it does make a significant improvement in demulsibility and both thermal and oxidation stability of the resulting Group I base stock.

V. CONVERSION PROCESSING

Hydroprocessing is a general term given to using a catalyst with hydrogen to convert less desirable crude fractions into quality lubricants. More specific terms are given these processes based on reaction severity according to temperature, pressure, and the amount of hydrogen present (Table 2.7). Hydrofinishing, at low severity, is typically stabilizing base stock and has very little reaction effect. Hydrocracking is at the other extreme, where high severity operation creates not only high-quality lube oil, but also gasoline, diesel, and lighter hydrocarbons. Hydrotreating severity falls somewhere between finishing and cracking, and is often used to condition a process stream. For example, hydrotreating is used to remove sulfur from a stream before it enters a process unit containing a noble metal catalyst that is very susceptible to poisoning by sulfur.

Hydroprocessing technology changed base oil refining technology from a process involving limited physical separation to an exceptional chemical operation. Conversion processing, in its various forms, is essential in turning crude oil into the high-quality Group II and Group III base stocks needed to meet the increasing performance demands of today. When comparing single viscosity grades, these base stocks have much lower volatility and better cold temperature performance capability than Group I stocks.

A diagram of the steps in conversion processing is shown in Figure 2.15. The first step in the conversion processing of vacuum gas oil and DAO is to pass it through a high severity *hydrocracker*

TABLE 2.7
Hydroprocessing Severity, Purpose, and Effect

Process →	**Hydrofinishing**	**Hydrotreating**	**Hydrocracking**
Process severity	Low	Medium	High
Purpose	Remove impurities, saturate olefins, stabilize color	Improve oxidation stability, reduce heteroatoms	Crack molecules, remove S, N, and aromatics
Processing effects			
Paraffins	No reaction	No reaction	Cracking
Naphthenes	No reaction	No reaction	Ring opening
Aromatics	Partial saturation	Partial saturation	Saturation
Olefins	Saturation	Saturation	Saturation
Sulfur removal	Some	Some	Complete
Nitrogen removal	Little	Some	Complete

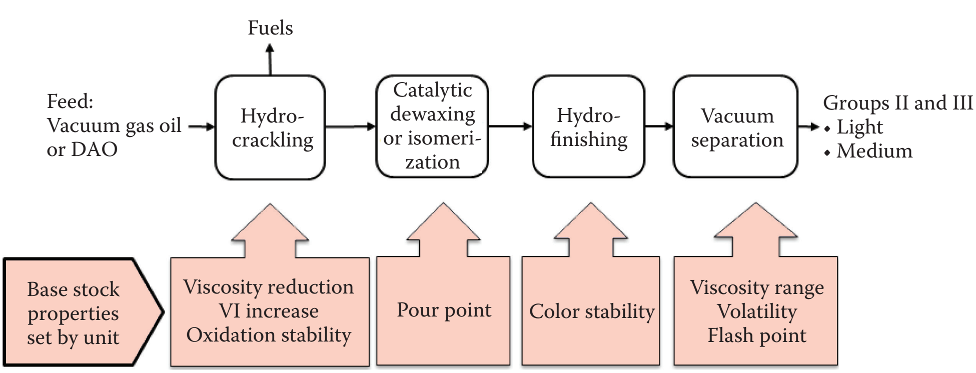


FIGURE 2.15 Conversion process used to make Group II and III base stocks.

to produce a waxy oil. Next, the oil from the hydrocracker is *catalytically dewaxed*. In this process, waxy paraffins are converted into isoparaffins that exhibit good low temperature performance. Finally, this is followed by hydrofinishing and the subsequent distillation into the desired viscosity grades.

A. Hydrocracking

Hydrocracking has clearly replaced solvent extraction as a preferred means for converting crude into paraffinic feeds for base stock production. Vacuum gas oil or DAO is reduced to a lower molecular weight and a higher hydrogen content in a complex process. Significant reactions that take place in hydroprocessing are aromatic ring saturation, naphthenic ring opening, olefin saturation, cracking of paraffins, and removal of sulfur and nitrogen. Refining conditions are carefully controlled because there are optimum conditions for the manufacture of high-quality lubes. Pushing conditions beyond the optimum can actually cause a severe drop in base stock quality.

Hydrocracking is typically done in a reactor with a catalyst that is packed in separate beds arranged along the reactors' length. Because the hydrocracking reaction generates large quantities of heat, quench zones are arranged between the various catalyst beds where hydrogen can be fed to control reaction temperatures to better control the reaction and its severity. Consideration needs to be given to feed composition, catalyst selection, capability of downstream processing, and unit operating conditions of temperature, pressure, and both hydrogen flow and consumption. To convert crude into high-performance base stock, it is necessary to use hydrogen and a catalyst under the severe hydrocracking conditions of high temperature and pressures (as high as 3000 psi or 20,684 kPa). Proper catalyst selection is key to both good yield and long catalyst life.

A single multifunctional catalyst is often used for base stock hydroprocessing, serving both aromatic saturation and cracking. Aromatic saturation occurs at a junction between an active metal and the catalyst base. In turn, cracking is controlled by the acidity of the catalyst base itself. Acid strength varies according to the mixture of materials in the catalyst base. Catalyst acidity has a significant effect on product output. If acidity is too high, it will result in the production of an excess of lower value light products. Hydrocracking catalysts are also sensitive to excessive contaminants in the feed. If necessary, nitrogen and sulfur may be removed by treating the feed with a less sensitive catalyst before it is hydrocracked. Some base stocks may be produced from these two-stage hydrocrackers.

Group II and Group III saturates levels are typically well above 90%, with most of the aromatics undergoing saturation during hydrocracking. Where the goal is to maximize lube production, conversion to light fuel products is limited to about 30% of the feed, leaving a greater portion for base oil. Therefore, in lubes hydrocracking, there is a relatively high content of low VI naphthenic material exiting the hydrocracker in combination with a mix of paraffins. In contrast, where the goal is to maximize fuel production, more severe hydrocracking is necessary. As a result, fuel hydrocracking produces a waxy, paraffinic feed that has a lower naphthenic content, making it ideal for producing high VI Group III base stocks.

B. Catalytic Dewaxing

The lube streams from hydrocracking contain waxy paraffinic material that must be eliminated to improve low temperature properties. In conversion processing, a dewaxing catalyst is used along with high pressure hydrogen. Early catalytic dewaxing processes worked by simply cracking waxy normal paraffins into smaller molecules, resulting in loss of yield. However, by using advanced catalyst technology, dewaxing can take place by converting normal, straight-chain paraffins into lube-quality branched isoparaffins. In contrast to solvent dewaxing, dewaxing by isomerization results in higher performance base stocks at higher product yields.