

SYNTHETIC LUBRICANTS:

Among their many uses, they've helped take spacecraft to the stars and back. But a galaxy of misinformation still surrounds these unique materials.

By Charles Barrett, CLS

Perception vs. Reality

Synthetic fluids suitable for use in lubricants have been around for more than 125 years. The first fluids, solely consisting of hydrocarbon molecules, were

produced by the chemists Charles Friedel and James Mason Crafts in 1877.¹ In 1929 the Standard Oil Co. of Indiana produced and attempted to market a synthetic hydrocarbon oil but was not commercially successful due to a lack of demand.²

At five plants during World War II, Germany produced around 5,400 metric tons (mt) per month of hydrocarbon and non-hydrocarbon synthetic base oils for use in lubricants during their peak production period. The vast majority of these base oils were synthetic hydrocarbon bright stock for use in aviation lubricating oils.³ Although the attributes of synthetic-based lubricants were well known by the 1950s, their use remained limited, primarily in aviation and specialized applications such as cylinder lubricants for high-pressure reciprocating compressors through the 1960s.

In 1972, according to Les Rudnick and Ronald Shubkin, Amsoil Corp. became the first to market a full synthetic API-certified motor oil. These were 100% diester-based and were followed in late 1977 by a full synthetic 10W-40 motor oil based on a polyalphaolefin (PAO) and ester blend.² The commercial success of these products and others that followed, including those produced and marketed by major oil companies, provided the impetus for the accelerated acceptance of synthetic lubricants at both the consumer and industrial level.

The result was that in the early 1980s,

almost 60 years after the first attempt to commercialize synthetic hydrocarbon molecule base oils, synthetic base oils finally achieved recognition beyond specialty products as economically viable alternatives to mineral base oils for use as lubricants. Today lubricants based on fully synthesized fluids are routinely used in applications ranging from the exotic (spacecraft) through demanding industrial applications like continuous casters in steel mills, in the main gearboxes of wind turbines and in passenger cars and heavy-duty trucks.

The exact size of the global market for lubricants varies depending on the data source. Various lubricants and base oils industry research organizations estimate the 2006 market was between 39 million mt to 41 million mt. The article "Global Supply: Links and Kinks," published in the April 2007 *Lubes 'N' Greases* magazine, quotes the 2006 global lubricants market to have been 40 million mt.

The size of the global synthetic lubricants market also is somewhat elusive. Several estimates for the global synthetic lubricants market peg its growth since 1999 as being up by more than 100%, increasing from a base range of 0.65 million mt to 0.75 million mt (1.4% to 1.8% of the 1999 total global lubricants market). Their use in 2006 ranged



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from 1.2 million mt to 1.6 million mt (3.0% to 3.8% of the total global lubricants market) depending on the source. The size of the synthetic lubricants market may be a very small portion of the overall global lubricants market. Yet, again depending on the source, it is projected to continue to grow strongly through 2010-2012 while the use of mineral-based lubricants is expected to stay relatively flat or decline as it has over the past decade or more.

The major portion of the expanding synthetic lubricants market is increased demands within the consumer and commercial ground transportation market. Motor oils capable of improving fuel economy, lowering emissions or being more compatible with emission control devices and providing longer service life is globally the biggest subsegment of this market.

However, demands for better fuel economy and more durable driveline lubricants, such as those for final drive gearing, manual, semiautomatic and automatic transmissions, also has been expanding. Even though the ground transportation market may represent the giant's share of synthetic lubricants, many industry reports and my investigations concur that the global industrial synthetic lubricants segment has grown at greater annual percentage rates than the transportation segment.

With all of the positive growth aspects of the synthetic-based lubricants market, why then do these products in many instances continue to be shrouded with misconceptions by potential as well as existing users? The remainder of this article addresses these and other issues, including: What are these lubricants? What benefits do they offer to lower the overall cost of ownership of mechanical systems? What are their potential weaknesses? When can they be cost-effective replacements for conventional mineral oil-based lubricants?

What is a synthetic?

What constitutes whether a lubricant is synthetic-based or not? If it's a fluid lubricant like a motor oil or gear oil, individuals typically respond that the oil itself is a synthetic material. Likewise with

grease lubricants, the typical response is the oil component is a synthetic material. Are these responses correct? The definition of a synthetic may be of help.

Random House Webster Concise College Dictionary defines "synthetic" as (1.) of, pertaining to, proceeding by or involving synthesis. (2.) pertaining to or denoting compounds, materials, etc., formed through a chemical process by human agency as opposed to those of natural origin.

There are a great number of fluids produced by synthesizing specific molecules into new repetitive molecules with known chemical, physical and basic performance properties that are well suited as engineered/designer base oils and blendstocks for lubricants. A partial list of family types includes:

- Alkyl-naphthalenes
- Dialkylbenzenes
- Dibasic Acid Esters
- Fluorinated Compounds
- Fluorosilicones
- Multiply-Alkylated Cyclopentanes (MACs)
- Neopolyol Esters
- Polybutenes
- Polyalkylene Glycols
- Polyalphaolefins
- Phosphate Esters
- Polyphenyl Ethers
- Polyvinylethers
- Silicate Esters
- Silicones.

Each of these and synthesized oils potentially may be produced from a variety of feedstocks and/or through the use of varying processes. The result is that even within a specific "family" of synthesized oils, properties may vary.

Lubricant formulators may select a specific brand of synthetic base oil or blendstock for an assortment of reasons. The formulator may require specific physical and performance properties or compatibility with additives that are expected to be included in the formulation. The finished lubricant may be a blend of two or more synthetic fluids or include mineral oil to achieve targeted performance or market point objectives. Or, possibly, compatibility with the finished lubricant's intended application is the principal driver. Then, of course, there are

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always just cost considerations.

If this implies that formulating synthetic lubricants is more complex than formulating mineral oil-based lubricants, not so. This decision-making process is not isolated to synthetic lubricant formulations. It applies to the development of new or the optimization of existing mineral oil or synthetic lubricants when the formulator is allowed or encouraged to consider all options to produce products that meet the desired physical and performance criteria and can be a commercial success.

It should be understood that formulating higher-performing, more durable mineral oil lubricants has become and continues to be increasingly challenging. Mineral base oils, solvent neutrals and bright stocks that were in high demand and readily available a decade ago now may be in short supply, and some may no longer exist.

Demands for higher-performing, more durable mineral oil-based lubricants has influenced the development of increasingly improved and more efficient refining processes. Several producers employing these processes have claimed that certain top-end grades of their base oils have properties rivaling those of some fully synthesized products—especially those used in the formulation of ground transportation and lower viscosity grade industrial lubricants.

To add complexity to what is meant by a synthetic lubricant, during the 1990s newly introduced highly refined mineral base oils began being formulated into motor oils as replacements for polyalphaolefins (PAOs). The base oils involved are categorized as API and ACEA Group III oils. API in the U.S. and ACEA (the European Automobile Manufacturers Association) in the European Union have established categories based on sulfur content, saturates content and viscosity index for Groups I, II & III, a Group IV for all PAOs and a Group V for all other base oils not included in Groups I, II, III or IV.

ACEA also includes a Group VI for all poly-internal olefins (PIOs). After long drawn-out debates and arguments, in 1999 the North American Council of Better Business Bureaus, National Advertising, was asked to make a ruling on what constituted a synthetic lubricant. Its decision was that products formulated with API Group III mineral oil basestocks may be labeled as synthetic lubricants in North America. This has been the case ever since. In the EU efforts continue by lubricant marketers to label their products, as is allowed in North America. To my knowledge, these efforts are ongoing and only products containing fully synthesized oils may be labeled as a full synthetic.

Other than generalizing a broad range of products, readers should have a better understanding why using the term “synthetic” is ambiguous when describing lubricants. Hopefully the following will help simplify matters.

Of the broad range of fully synthesized base oils and their variants being produced and marketed in volumes ranging from modest to very large, only a few are representative of the vast bulk of the global synthetic lubricants market. Although regional variations exist, typically polyalphaolefins are the most prevalent, with dibasic acid esters, neopolyol esters, polyalkylene glycols and phosphate esters constituting the majority of the remaining market for fully synthetic base oils and blendstocks. Alkyl-naphthalenes and polybutenes find significant roles as additives and trim stocks. The remaining types of fully synthesized lubricant grade oils are typically used in small to modest volume applications such as specialty lubricants.

Potential benefits

It would make it easy if we could simply produce a generic list of strengths and weaknesses for lubricants produced with fully synthesized base

Synthetic case study: U.S. paper mill



Facility:

Paper mill in the Northeast United States.

Application:

Paper machine Beloit Controlled Crown Roll (CCR) calendar stack.

Conditions:

Typical paper machine finish end conditions: humid, very warm, dusty, etc. High internal pressure sliding friction forces and high-speed, heavily loaded rolling element bearings.

Objective:

Increase CCR PLI loads and, thus, overall paper machine throughput. Reduce paper machine maintenance, including extended oil drain cycles.

Parties Involved:

Paper mill maintenance personnel. Synthetic lubricant supplier representatives.

Lubricants:

Previous: Premium ISO VG 220 mineral-based paper machine oil. New: Fully synthesized ISO VG 220 Synfilm® GT synthetic circulating oil based on PAO containing a proprietary additive package.

Monitoring:

Temperatures of oil circulating system to and from the roll flow of oil within roll circulating system. Circulating oil system cooling water temperatures and flow CCR PLI paper machine speed and throughput.

Results:

Average temperature of oil returning from CCR reduced by 18 C/32 F. PLI load increased from 650 to 873 (+34.3%). Throughput increased from an average 488 mpm/1600 fpm to 543 mpm/1780 FPM (+11.2%). Calculated reduced energy loss within CCR system of 97.8 kW per hour.

Source: Royal Purple, One Royal Purple Lane, Porter, Texas. Phone: (281) 354-8600, Fax: (281) 354-7600, www.royalpurple.com.

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oils, but that is not representative of reality. As commented earlier, each synthetic base oil family type and its variants have specific properties. Some of these properties are inherent as a result of their basic chemistries. Others are intentionally engineered in or are the result of feedstock and process variations.

Base oils may represent the major component of most lubricants, especially oils, but it is not the only component. Additive packages can and usually do have dramatic effects on the performance of lubricants in service. With greases, the thickener system also plays a major role on performance, as do fillers if they are used. The primary value of a table or list providing basic properties of neat base oils is that it may be used as an indicator of how they may behave over a range of ambient and operating conditions. These tables and lists are available in numerous publications and references. *The Tribology Data Handbook*, sponsored by STLE and published by CRC Press, *The Lubrication Engineers Manual, Third Edition*, published by AIST, and *Synthetic Lubricants and High-Performance Functional Fluids, Second Edition Revised & Expanded*, published by CRC Press, are just three examples that contain excellent background as well as details about synthetic lubricants including their basic properties.

As with all lubricants, selecting the correct synthetic lubricant for a specific application or a group of similar applications and operating conditions is critical to successful, cost-effective results. What properties do synthetic lubricants have that may be different than those of mineral oil lubricants that would make them the product of choice for a specific application, a group of applications within a specific range of equipment types or operating conditions or for use as the primary lubricants in a manufacturing facility?

Being engineered products, fully synthesized base oils can offer chemical, physical and performance properties that can allow lubricant formulators the opportunity to produce products with specific capabilities. Some of these base oils possess very high to exceptionally high viscosity indices, making them very good candidates for use in applications such as gearboxes

or circulating oil systems subjected to very wide operating or low temperature startup conditions.

Others have poor viscosity indices but, due to excellent thermal and oxidative stability, excel at resisting aging and forming deposits when exposed to high operating temperatures. They can be superior bases on which to build high temperature conveyor chain lubricants. Some have unique inherent properties such as polyalkylene glycols that have excellent affinity to cupric metals, bronzes for example. This and very good lubricity makes them very good lubricants for use in high sliding action applications such as worm gears.



Synthetics such as polyolesters and dibasic acid esters, and in particular phosphate esters acid esters, can have very high flash and fire points, making them products of choice when formulating non-water-based fire-resistant hydraulic and circulating oils. Some synthetics may have high flash and fire points plus very low volatility, making them ideal candidates for applications subjected to extended or continuous operation at high temperatures such as motor oils and lubricants for use in flooded rotary compressors.

Dibasic acid esters, like natural esters found in vegetable oils containing oleic acid, can be readily biodegradable and, when formulated with suitable additives, can produce high performance, durable, environmentally less objectionable lubricants. Some of the lower viscosity polyalphaolefins reportedly have good to very good biodegradability properties and have been used in blends with esters to produce similarly durable, environmentally less objectionable lubricants.

Depending on the fully synthesized base oil, some inherently have better viscomet-

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ric, antiwear, extreme-pressure, thermal stability, oxidative stability, thermal shock resistance, volatility or lubricity properties in any combination over Group I, II or III base oils. Some have demonstrated the ability to depress parasitic losses within mechanical components and systems resulting in the reduction in the energy input required to accomplish the same amount of work compared to those achieved with mineral oils. Granted, the improvements in mechanical efficiency contributable to the use of the fully synthesized base oil alone may be small. However, if the input energy source contributes to greenhouse gas (GHG) emissions, the combined overall energy cost savings and value of GHG, e.g., CO₂, credits can be substantial.

As stated previously, the fully synthesized base oil may be the major component but is not the only component of a synthetic lubricant. Additives, blendstocks and/or trim stocks can play a key role in how the finished product will perform under various operating conditions. As with mineral oil formulations, lubricants formulated with synthetic base oils often require additives to enhance specific properties to achieve the overall level of performance required from the finished lubricant.

When synthetic lubricants started to become commercial successes, their formulators had to rely on their experiences with mineral oil products and additives used in their formulation. As a result, end-users of some of the earlier products had hit-and-miss experiences with synthetic lubricants. Most readers have probably heard one or more horror stories about how synthetic motor oils were “no good” for engines with more than 20,000 or 30,000 miles since they cause seals to leak and engines to become oil burners. There were also the stories of how synthetic gear oils or flooded rotary screw compressor oils or circulating oils had unpredictable service lives. The oils were

good one day, and the next day the equipment shut down and the oil had turned thick and dark. Some of these stories obviously had merit and some have become myths. More on these and other experiences shortly.

Additives and additive technologies available to the early formulators of synthetic lubricants were limited almost exclusively to those designed for use in mineral oil lubricants. Unfortunately these additives did not always behave or produce the intended results when used in fully synthesized base oils.

Over the years formulators have learned through trial and error how to make additives respond and perform as intended in these base oils. Several have, in effect, become internal additive producers taking different materials from one, two or more additive suppliers and producing unique proprietary packages that are highly stable and produce levels of performance likely not available using off-the-shelf packages. Some of these proprietary additive systems reportedly greatly increase the load-carrying, antiwear, antiscuff or friction-reduction properties of the lubricants that contain them.

Claims for the superior performance of a lubricant or proprietary lubricant additive system are nothing new, whether they are well documented through independent test results, testimonials and endorsements or not. For many years formulators and marketers of synthetic and mineral oil-based lubricants alike have done this, more typically independents rather than the majors. Ultimately it is the benefits users of synthetic lubricants receive that are most important. The synthetic lubricant market segment has matured and with that has come a great deal of knowledge based on hands-on experiences in how to formulate products that can deliver the overall lowest cost of equipment ownership

Synthetic case study: U.K. petrochemical plant



Facility:

Petrochemical plant in the United Kingdom.

Application:

Two 20 MW, six-stage integral gear-driven turbo compressors handling process air.

Conditions:

Separate building with dedicated substation providing electricity from power grid to compressors. 24/7 operation whenever possible.

Objective:

Determine if and how much electrical energy reduction could be achieved by changing lubricants from mineral oil-based to full synthetic. If energy reduction is obtained, determine its impact on greenhouse gas emissions (source of electricity being a coal-fired generating plant).

Parties Involved:

Customer (compressor owner and operator). Lubricant supplier (both existing mineral oil and new synthetic lubricants). Compressor OEM independent consultant.

Lubricants:

Previous: BP Energol® TH-HT mineral-based turbine oil with a proprietary additive package. New: BP Enersyn RC-S® synthetic oil based on PAO with a proprietary additive package. Lubricant capacity of 10,000 liters for each compressor.

Monitoring:

Automated data logging by control system regulating individual compressor load and power and balancing load and power between both compressors. Automated data logging of oil, bearing and cooling water temperatures. Automated data logging of bearing vibration levels.

Results:

1.57% (0.265 MW) average reduction in electrical consumption under normal operating conditions. A calculated 450 mt annual reduction in greenhouse gas emissions. Corresponding reductions in bearing operating temperatures. Corresponding reductions of vibration levels.

Source: Castrol Industrial North America Inc., Industrial Lubricants & Services, 150 West Warrenville Road 605-3E, Naperville, Ill. 60563 (USA). Phone: (877) 641-1600, Fax: (877) 648-9801, www.castrol.com/industrial.

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when used in appropriate applications and as an integral component of proactive maintenance practices. The primary benefits today's fully synthesized base oil formulated lubricants can offer include but are not limited to:

- A. Extended component parts life.
- B. Extended lubricant drain and refill or lubricant replenishment cycles.
- C. Elimination of semiannual changes in fluid lubricant viscosity grades or grease grades to maintain operation between changes in summer and winter ambient temperatures.

A + B + C =

- less scheduled and unscheduled downtime, resulting in improved equipment reliability and availability.
- fewer replacement parts.
- reduced lubricant inventories and associated procurement, handling and disposal costs.
- reduced exposure of personnel to potential safety risks associated with time-pressed tasks performed during unscheduled outages.
- potentially reduced exposures to environmentally related issues associated with lubricants entering wastewater systems or their disposal.

D. Reduced component or overall mechanical system operating temperatures.

- E. Reduced vibration levels related to components operating in the mixed film or thin film lubrication regimes.

- F. Reduced mechanical system parasitic losses such as drag induced by fluid friction, pumping losses, windage, etc.

D + E + F =

- strong indicators and contributors of/to mechanical efficiency, reflected in reduced input energy to produce an equal amount of throughput or increased throughput with an equal consumption of energy.

Potential weaknesses

As with their potential benefits, synthe-

tic lubricants also have potential weaknesses that vary between the fully synthesized base oils used in their formulation. Some of these weaknesses are inherent with the chemical and physical properties of the base oils and, at least, currently have not to my knowledge been overcome. Examples include:

- When esters entrain water and are exposed to heat they tend to hydrolyze, splitting back into an acid and alcohol. Depending on the chemistry of the ester, this process can be minimal or severe. The end products of this process are acids with the potential of corroding mechanical system components.
- Some of these base oils such as polyalkylene glycols and phosphate esters are more dense than water and can settle in water-retention systems like those used in waste treatment or metal-working fluids.
- Many neat polyalphaolefins, when exposed to constant high temperatures in a thin film state, may oxidize and potentially form sticky varnish-like deposits.
- Silicones are extremely tenacious and attach to surfaces they contact. They can create problems such as "fisheyes" or blistering in coating processes such as painting.
- Incompatibilities with paints, coatings, sealants and elastomers can vary between finished synthetic lubricants, even those using similar fully synthesized base oil chemistries.
- Incompatibilities between synthetic base oil types and mineral oils. For example, esters and polyalphaolefins in general are fully compatible among themselves and mineral oils, but polyalkylene glycols are immiscible with mineral oils, polyalphaolefins and most esters.
- Initial purchase prices are typically four, six or more times expensive than commodity-grade mineral oil lubricants. Their continued use can become difficult to justify unless the benefits they generate or have generated are well documented and there is support from those responsible for cost control.

Even within a specific "family" of synthesized oils, properties may vary.

When are they cost-effective?

It is easier to address when synthetic lubricants can be cost-effective alternatives to mineral-based lubricants by clarifying when they typically *are not* cost-effective. This includes:

- Applications where reservoirs, sumps or equipment housings are subject to more than minimal leakage. No matter how well the lubricant may perform, it is not good practice to allow it to continuously enter a waste stream. Minimize or eliminate leaks whenever possible before attempting to justify the use of synthetic lubricants. An exception may be in severe applications subject to exposure to sources of ignition and the use of a synthetic lubricant such as a phosphate ester fire-resistant hydraulic fluid.
- Applications subject to the ingestion of sufficient amounts of environmental or process contaminants that will rapidly degrade the lubricant or otherwise cause it to frequently become unsuitable for continued use. Exceptions include when the potential value of an extension of the service life or reliability of the equipment achieved justifies the use of a synthetic lubricant.
- Lightly loaded, infrequently utilized non-critical path equipment. Exceptions include when this equipment requires minimal amounts of lubricant and/or their exclusion would negatively impact consolidation of lubricants or would increase the potential of the inadvertent use of the incorrect lubricant in critical path equipment.
- Applications or areas where little if any historical documentation exists on equipment performance, maintenance or reliability or it is not possible to establish a sufficient amount of baseline data that will be accepted as support of the results data after peer-review.

In reality, lubricants based on fully synthesized base oils are available that will perform as well and typically better than mineral oil-based lubricants for all but a limited number of applications. The demand for more efficient, more durable, reduced-maintenance equipment is apt to continue in increasingly higher power densities. Coupled with the growing acceptance of the lubricant being an integral component of equipment design, synthetic lubricants will most probably be called on more and more to produce the required results.

For equipment owners, the decision to use a synthetic lubricant instead of a mineral oil product will likely remain one of initial purchase price vs. overall cost of use or possibly for complying with warranty requirements. In many personal use applications, peace of mind or pride in ownership will remain a major driver.

For a multitude of reasons, the global market for synthetic lubricants is predicted to increase well into the foreseeable future. <<

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Synthetic case study: U.S. heavy-duty truck



Facility:

Class 8 Heavy-Duty Truck Test, Southwest Research Inc., San Antonio, Texas.

Application:

Heavy-duty truck rear drive axle, synthetic axle lubricant.

Conditions:

Typical on-highway heavy-duty truck application. Heavy Payload—76,000- pound gross vehicle weight, normal highway speeds.

Objective:

Determine if fuel economy benefits could be achieved through axle lubricant in a controlled test and quantify those benefits.

Parties Involved:

Southwest Research Inc. personnel. Synthetic lubricant supplier representatives.

Lubricants:

Previous: Market General Synthetic 75W-90 and mineral-based axle lubricants. New: Fully synthetic specially designed Emgard® FE-Fuel Efficient 75W-90 axle fluid.

Monitoring:

Fuel consumption was precisely weight measured and statistically controlled from baseline run to final comparison run.

Results:

Average fuel economy improved over 1% when comparing the new, specially designed lubricant to both the market general synthetics and mineral heavy-duty truck axle lubricants.

Source: Cognis Corp., Functional Products, Research and Technology, 5051 Estecreek Drive, Cincinnati, Ohio 45232-1446. Phone: (513) 482-3000, Fax: (513) 482-5503, www.cognis.com.