

Chapter 17

SYNTHETIC LUBRICANT BASE STOCK PROCESSES AND PRODUCTS

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1. INTRODUCTION

This chapter reviews the product and process for synthetic base stocks produced from chemicals of well-defined chemical structures and in processes tailored to optimize important properties and performance features. These synthetic base stocks are critical components used in the formulation of many synthetic lubricants. (In this chapter, we use “synthetic base stock“ to represent the base fluid and “synthetic lubricant“ to represent formulated, finished lubricant product.)

At the start of this chapter, we briefly discuss the background and the driving force for using synthetic lubricants. The major part of the chapter discusses the key synthetic base stocks - chemistry, synthesis processes, properties, their applications in synthetic lubricant formulation and advantages compared to petroleum-derived base stocks.

Many U.S. base oil manufacturers and formulators include some Group II+ and Group III base stocks as synthetic, as their manufacturing process includes varying degrees of chemical transformation. These base stocks are usually produced by hydroprocessing or hydroisomerization, which is typically part of a refining process¹. Discussion of these hydroprocessed base stocks can be found in the previous chapter. In this chapter, we limit discussion to those synthetic base stocks produced from chemicals of well-defined composition and structure.

1.1 Why Use Synthetic Lubricants?

Synthetic lubricants are used for two major reasons:

- When equipment demands specific performance features that can not be met with conventional mineral oil-based lubricants. Examples are extreme high or low operating temperature, stability under extreme conditions and long service life.
- When synthetic lubricants can offer economic benefits for overall operation, such as reduced energy consumption, reduced maintenance and increased power output, etc.

Conventional lubricants are formulated based on mineral oils derived from petroleum. Mineral oil contains many classes of chemical components, including paraffins, naphthenes, aromatics, hetero-atom species, etc. Its compositions are pre-determined by the crude source. Modern oil refining processes remove and/or modify the molecular structures to improve the lubricant properties, but are limited in their ability to substantially alter the initial oil composition to fully optimize the hydrocarbon structures and composition. Mineral oils of such complex compositions are good for general-purpose lubrication, but are not optimized for any specific performance feature. The major advantages for mineral oils are their low cost, long history and user's familiarity. But this paradigm is now changing.

The trend with modern machines and equipment is to operate under increasingly more severe conditions, to last longer, to require less maintenance and to improve energy efficiency. In order to maximize machine performance, there is a need for optimized and higher performance lubricants. Synthetic lubricants are designed to maximize lubricant performance to match the high demands of modern machines and equipment, and to offer tangible performance and economic benefits.

1.2 What Is a Synthetic Base Stock?

Synthetic lubricants differ from conventional lubricants in the type of components used in the formulation. The major component in a synthetic lubricant is the synthetic base stock. Synthetic base stocks are produced from carefully-chosen and well-defined chemical compounds and by specific chemical reactions. The final base stocks are designed to have optimized properties and significantly improved performance features meeting specific equipment demands. The most commonly optimized properties are:

- **Viscosity Index (VI).** VI is a number used to gauge an oil's viscosity change as a function of temperature. Higher VI indicates less viscosity change as oil temperature changes - a more desirable property. Conventional 5 cSt mineral oils generally have VIs in the range of 85 to 110. Most synthetic base stocks have VI greater than 120.

- **Pour point and low temperature viscosities.** Many synthetic base stocks have low pour points, -30 to -70°C, and superior low-temperature viscosities. Combination of low pour and superior low-temperature viscosity ensures oil flow to critical engine parts during cold starting, thus, offering better lubrication and protection. Conventional mineral oils typically have pour points in the range of 0 to -20°C. Below these temperatures, wax crystallization and oil gelation can occur, which prevent the flow of lubricant to critical machine parts.
- **Thermal/oxidative stability.** When oil oxidation occurs during service, oil viscosity and acid content increase dramatically, possibly corroding metal parts, generating sludge and reducing efficiency. These changes can also exacerbate wear by preventing adequate oil flow to critical parts. Although oil oxidation can be controlled by adding antioxidants, in long term service and after the depletion of antioxidant, the intrinsic oxidative stability of a base stock is an important factor in preventing oil degradation and ensuring proper lubrication. Many synthetic base stocks are designed to have improved thermal oxidative stability, to respond well to antioxidants and to resist aging processes better than mineral oil.
- **Volatility.** Synthetic base stocks can be made to minimize oil volatility. For example, polyol esters have very low volatility because of their narrow molecular weight distribution, high polarity and thermal stability. Similarly, careful selection and processing of raw materials can influence the finished properties of polyalphaolefins (PAO) base stocks.
- **Other properties,** including friction coefficient, traction coefficient, biodegradability, resistance to radiation, etc. can be optimized for synthetic base stocks as required for their intended applications.

1.3 A Brief Overview of Synthetic Lubricant History

Significant commercial development of synthetic lubricants started in the early 1950's with the increased use of jet engine technology². Jet engines must be lubricated properly in extremely high and low temperature regimes where mineral lubricants could not adequately function. Esters of various chemical structures were synthesized and evaluated. Initially, dibasic esters were used as base stock. Later, polyol esters with superior thermal/oxidative stability, lubricity and volatility were developed to meet even more stringent demands. These polyol esters are still in use today.

Another early application that demanded the use of synthetic lubricants came in the mid-1960s during oil drilling in Alaska where conventional mineral oil lubricants solidified and could not function in the severe Alaskan cold weather³. Initially, a synthetic lubricant based on an alkylbenzene base stock of excellent low temperature flow properties was used in the field. This base stock was soon replaced by another base stock with better overall properties, namely polyalphaolefins (PAO).

Research on PAO began at Socony-Mobil in early 1950s⁴. The early researchers recognized the unique viscometric properties that could be attained by the proper selection of starting olefins and reaction conditions in the PAO synthesis. After many years of continuous improvements in optimizing the compositions, processes and formulations, Mobil Corporation introduced a synthetic automotive engine oil, Mobil SHC™ in Europe in 1973, followed by a fuel-saving SAE 5W-20 Mobil 1™ in the US. The product was a commercial success and successive generations of Mobil 1™ continue to be the leading synthetic automotive crankcase lubricant today⁵.

Since the early introduction of synthetic lubricants in automotive and industrial applications, many products from numerous companies have followed. The total synthetic lubricant market in 1998 amounted to about 200 million gallons/yr, approximately 2% of the total lubricant volume⁵. However, it is estimated to grow at 5-10% per year, much higher than conventional lubricant (less than 2% per year). Although the volume of synthetic lubricants is relatively small compared to conventional lubricants, the overall economic impact from synthetic lubricants is much larger than just the volume number alone, since synthetic lubricants improve energy efficiency, productivity, reliability and reduce waste, etc.

2. OVERVIEW OF SYNTHETIC BASE STOCKS

Of the total world wide synthetic base stock volume, over 80% are represented by three classes of materials⁶

- PAO (45%)
- Esters, including dibasic ester and polyol esters (25%)
- Polyalkyleneglycol (PAG) (10%)

Other smaller volume synthetic base stocks include alkylaromatics, such as alkylbenzenes and alkyl naphthalenes, polyisobutylenes, phosphate esters and silicone fluids. Among these synthetic base stocks, with the exception of phosphate esters and silicones, the starting materials are all derived from basic petrochemicals - ethylene, propylene, butenes, higher olefins, benzene, toluene, xylenes, and naphthalenes, as illustrated in Figure 1.

As expected, the major producers of PAO, esters, PIB and alkylaromatics are integrated petroleum companies that supply conventional mineral oil base stocks and petrochemicals as well as various synthetic base stocks. PAG, phosphate esters and silicone fluids are manufactured by chemical companies that produce these fluids on a much larger scale mainly for other applications. Their use as lubricant base stocks is only a fraction of the total market. Table 1 summarizes the major synthetic base stock producers.

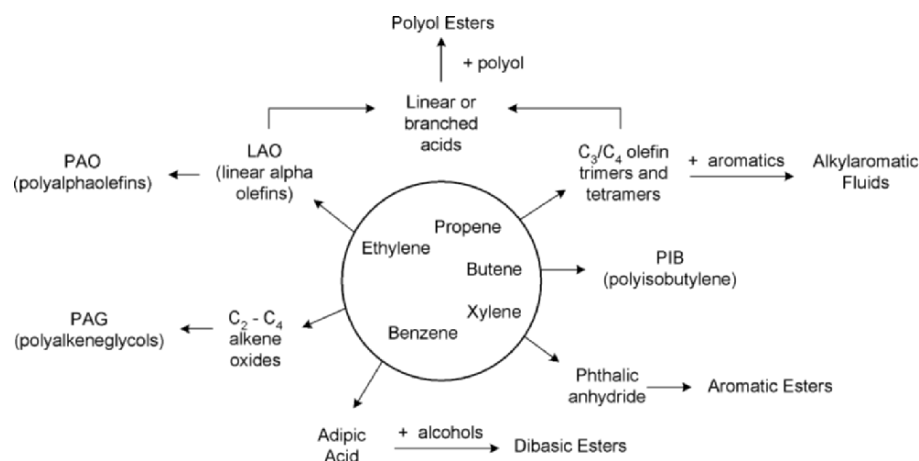


Figure 1. Most synthetic base stocks are derived from petrochemicals

Table 1. Summary of major synthetic base stocks and producers

Synthetic Base Stock	Major Manufacturer	Relative price*
PAO	ExxonMobil Chemical Co., BP, Chevron Phillips Chemical Co., Fortum	4
Dibasic ester	ExxonMobil Chemical Co., Henkel Corp., Hatco Corp., Inolex Chemical Co.	5
Polyol ester	ExxonMobil Chemical Co., Henkel Corp., Hatco Corp., Inolex Chemical Co., Kao Corp.,	7-10
PAG	Dow Chemical Co., BASF	4-10
Alkylaromatic	ExxonMobil Chemical Co., Pilot Chemical Co., Inolex Chem. Co.	4-8
Mineral oil	ExxonMobil, Motiva Enterprise, ChevronTexaco, Valero, BP, Shell, etc.	1

* Estimated relative price vs. Group I mineral oil

3. SYNTHETIC BASE STOCK - CHEMISTRY, PRODUCTION PROCESS, PROPERTIES AND USE

3.1 PAO

PAO with viscosities of 2 to 100 cSt at 100°C are currently produced and marketed commercially⁷. The low viscosity PAO of 4 to 6 cSt account for more than 80% of the total volume. The remaining are mainly medium to high viscosity products of 10 to 100 cSt.

3.1.1 Chemistry for PAO Synthesis

1-Decene is the most commonly used starting olefin for PAO (Figure 2). It is produced as one member of the many linear alpha-olefins (LAO) in an ethylene growth process, which yields C_4 to C_{20} and higher LAO according to the Schulz-Flory distribution⁸. Typically, 1-decene constitutes about 10-25% of the total LAO fraction, depending on the process technology.

To make PAO, the linear 1-decene is further polymerized using Friedel-Crafts catalysts to give C_{20} , C_{30} , C_{40} , C_{50} , and higher olefin oligomers.

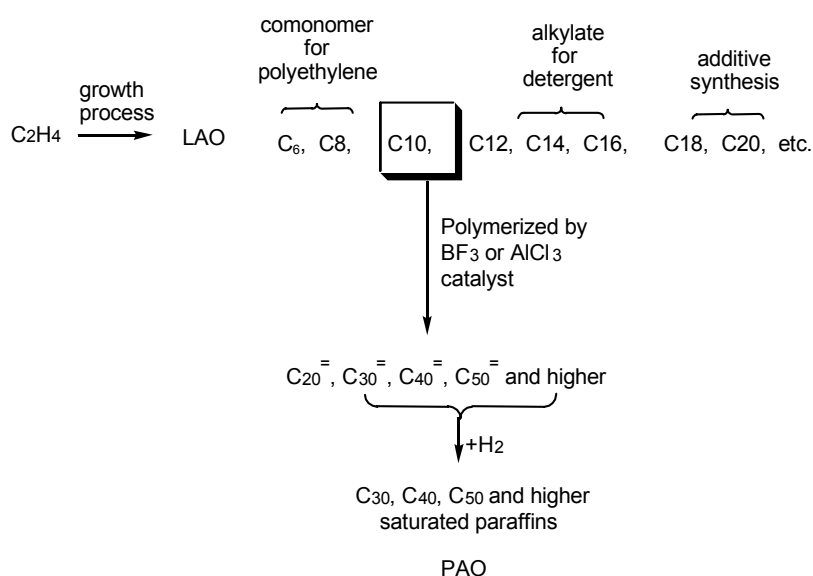


Figure 2. Reaction scheme for converting ethylene into PAO

The degree of polymerization depends on the type of catalyst used and reaction conditions⁹. Generally, BF_3 type catalysts give a lower degree of polymerization. By careful choice of co-catalyst types and reaction conditions, the BF_3 process produces mostly C_{30} to C_{50} oligomers that yield low viscosity base stocks of 4-8 cSt. $AlCl_3$ -based catalysts are more suitable for higher viscosity PAO synthesis because they produce oligomers with C_{60} , C_{70} and higher olefin enchainment species. If a C_{20} fraction is produced, it is usually separated and recycled. Fractions containing C_{30} and higher olefin oligomers are then hydrogenated to yield fully saturated paraffinic PAO.

PAO is a class of molecularly engineered base stock with optimized viscosity index, pour point, volatility, oxidative stability and other important lubricant base oil properties. Researchers at ExxonMobil have systematically synthesized polyalphaolefin oligomers of C_{30} to C_{40} by BF_3 catalysis and compared their lubricant properties, as summarized in Table 2.¹⁰

Table 2. Lubricant base stock property comparison: C₃₀-C₄₂ hydrocarbons made from different olefins

Name	Carbon Number	Kinematic Viscosity, cSt, at			Viscosity Index	Pour Point, °C
		100°C	40°C	-40°C		
Propylene decamers	C30	7.3	62.3	>99,000	70	--
Hexene pentamers	C30	3.8	18.1	7,850	96	--
Octene tetramers	C32	4.1	20.0	4,750	106	--
Decene trimers	C30	3.7	15.6	2,070	122	<-55
Undecene trimers	C33	4.4	20.2	3,350	131	<-55
Dodecene trimers	C36	5.1	24.3	13,300	144	-45
Decene tetramers	C40	5.7	29.0	7,475	141	<-55
Octene pentamers	C40	5.6	30.9	10,225	124	--
Tetradecene trimers	C42	6.7	33.8	Solid	157	-20

These data show that the oligomers made from propylene, 1-hexene and 1-octene have relatively low VI and very high viscosity at -40°C. Oligomers from 1-tetradecene have high VI but also have undesirable high pour point and are solid at -40°C. Oligomers from 1-decene have the best combination of high VI, low pour point and -40°C viscosity.

Historically, the market dynamics of LAO supply and demand further drove the trend toward the use of 1-decene as a raw material. Among all the major LAO from the ethylene growth process (Figure 2), C₆ and C₈ LAO are used as co-monomer in the linear low-density polyethylene production; C₁₂₋₁₆ LAO are used in the manufacture of linear alkylbenzene detergent; C₁₈ and C₂₀ LAO are used in additives. 1-Decene is not in high demand for other chemical manufacturing and its use as raw material for synthetic base stocks makes a perfect match. When 1-decene supply became tight, other LAO, such as C₈ and C₁₂, have been successfully incorporated with 1-decene as the starting olefins for PAO production. Since 2001, 1-decene supply has increased significantly due to several LAO expansion projects and new production coming on-line around the world¹¹.

The chemical composition of PAO is very simple. Using 4 cSt PAO as an example, it is made of ~ 85% C₃₀ and ~15% C₄₀ hydrocarbons. It has a narrow molecular weight distribution compared to typical 4 cSt mineral oils. The gas chromatograms in Figure 3 show that 4 cSt PAO has few low

molecular weight components of less than C_{30} that can degrade oil volatility, flash and fire point. Figure 3 also shows that the C_{30} fraction of PAO is not a single compound but a mixture of many isomers. This is because the PAO from BF_3 process contains many isomers, each with different types of branching¹². This irregular branching may be beneficial to some of PAO's low temperature properties, e.g. pour point.

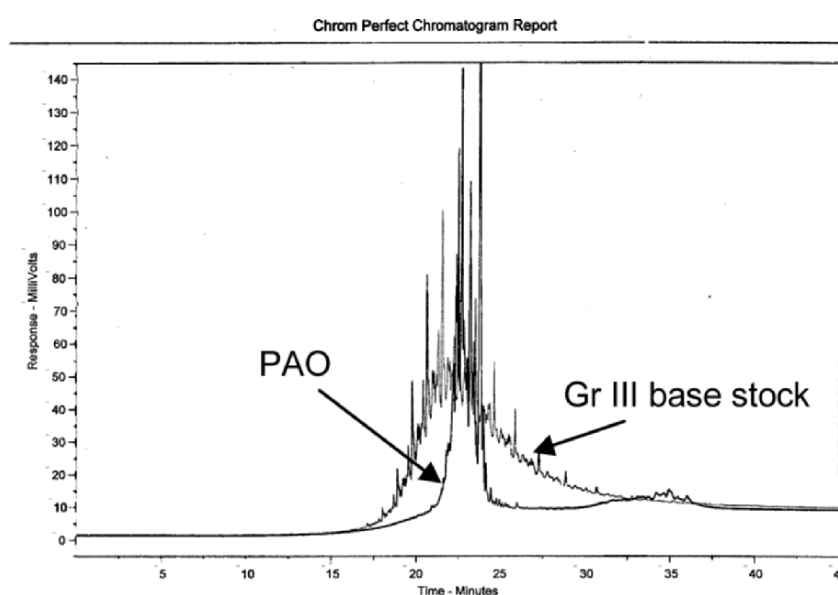


Figure 3. Gas chromatograph comparison of a 4 cSt PAO with a 4 cSt Group III base stock

3.1.2 Manufacturing Process for PAO

Commercial production of PAO using a BF_3 catalyst generally involves a multi-stage, continuous stirred tank reactor (CSTR) process⁹. In early production technology, the catalyst was destroyed with diluted aqueous alkali after polymerization. More recent patents disclosed improved processes using BF_3 catalyst recycle to reduce catalyst usage, minimize process waste and improve process economics¹³.

3.1.3 Product Properties

The physical properties of some commercial PAO are summarized in Table 3.⁷

Table 3. General product properties of commercial PAO from ExxonMobil Chemical Company

Fluid type	SHF-20	SHF-41	SHF-61/63	SHF-82/83	SHF-101	SHF-403	SHF-1003
Kinematic Viscosity @100°C, cSt	1.7	4.1	5.8	8.0	10.0	39	100
Kinematic Viscosity @40°C, cSt	5	19	31	48	66	396	1,240
Kinematic Viscosity @-40°C, cSt	262	2,900	7,800	19,000	39,000	--	--
Viscosity Index	--	126	138	139	137	147	170
Pour Point, °C	-66	-66	-57	-48	-48	-36	-30
Flash Point., °C	157	220	246	260	266	281	283
Specific Gravity @15.6°C/15.6°C	0.798	0.820	0.827	0.833	0.835	0.850	0.853

3.1.4 Comparison of PAO with Petroleum-based Mineral Base Stocks

PAO have different chemical compositions compared to mineral oil base stocks. The American Petroleum Institute (API) categorizes lubricant base stocks into five categories, designated Group I to V. The definition of each base stock group is summarized in Table 4.

Table 4. Definition of API category I to V lubricant base stock

Description	% Saturates	% Sulfur	VI
Group I (Conventional, solvent refined)*	<90	>0.03	80-120
Group II (Hydroprocessed)*	>= 90	</= 0.03	80-120
Group III (Severely hydroprocessed or isomerized wax)*	>= 90	</= 0.03	>=120+
Group IV Polyalphaolefins			
Group V All other base stocks not included in Group I, II, III or IV (e.g. esters, PAG, alkylaromatics, etc.)	--	--	--

* - comments in parentheses are not included in the original API definition

PAO is classified by itself as a Group IV base stock. In addition to the differences listed in Table 3, PAO also contains no cyclic paraffins, naphthenes or aromatics, whereas Group I, II and III base stocks contain different amounts of aromatics ranging from <1% to >40%¹⁴. With the increasing presence of aromatics and/or naphthenes, oxidative stability and low temperature properties of these fluids are typically degraded. Also, as shown earlier in Figure 3, PAO have discrete carbon numbers with relatively long linear hydrocarbon branches, whereas mineral base stocks contain a continuum of carbon number. As a result, PAO usually have lower volatility.

Table 5 compares the basic properties of low and high viscosity PAO versus Group I to Group III mineral oil base stocks.

Table 5. Typical property comparison of PAO with Group I to III mineral oil

	Low Viscosity				High Viscosity	
	Grp I	Grp II	Grp III	PAO	Bright stock	PAO stock
Kinematic Viscosity @100°C, cSt	3.8	5.4	4.1	4.1	30.5	100
Kinematic Viscosity @40°C, cSt	18	30	19	19	470	1,240
Viscosity Index	92	115	127	126	94	170
Pour Point, °C	-18	-18	-15	-66	-18	-30
Cold Crack Simulator @ -20°C, cP	--	--	750	620	--	--
Noack Volatility, wt%	32	15	14	12	--	--
Aniline point, °C	100	110	118	119	97	>170

- PAO have superior viscometrics properties compared to mineral oil base stocks.

Data in Table 5 show that PAO has higher VI and lower pour point than Group I and II base stocks. Compared to Group III base stocks, PAO has comparable VI, but much lower pour point and improved low-temperature viscosity as measured by Cold Cranking Simulator (CCS) viscosity at -20°C. In an actual engine oil formulation, this lower CCS viscosity observed with PAO results in a wider SAE cross-grade (5W-40) than with Group III base stock (10W-40)¹⁵. The lower low-temperature viscosity translates into better fuel economy during the engine warm up period.

- PAO has lower volatility.

Data in Table 5 show that PAO has lower volatility than Group I to III base stocks. This lower volatility is the result of the unique chemical compositions of PAO - 100% relatively linear paraffin, little low molecular weight hydrocarbons of less than C₃₀ (Figure 3). Low volatility is advantageous for decreased oil consumption and reduced emissions.

- PAO show intrinsic oxidative stability and excellent response to antioxidant additive treatment.

It has been demonstrated that the un-formulated PAO base stock treated with 0.5 wt% antioxidant resists oxidation for more than 2500 minutes in a standard rotary bomb oxidation test (RBOT, D2272 method). In comparison, similarly treated Group II and III base stock started to oxidize much earlier, at less than 800 or 1700 minutes, respectively¹⁶.

This oxidative stability translates into performance advantages in actual engine oil tests (Figure 4).¹⁵

Figure 4 shows that a fully formulated engine oil with PAO has much lower viscosity increase than with Group III or with Group I/II base stocks in standard length, 64-hour ASTM Sequence IIIIE engine test. In an extended-length, 256-hour test, the viscosity increase for PAO-based lubricant is still much less than the maximum increase allowable for this test. In contrast, Group III or Group I/II based engine lubricants become too viscous to measure. Performance advantages in fuel efficiency and oil consumption are also reported.¹⁷

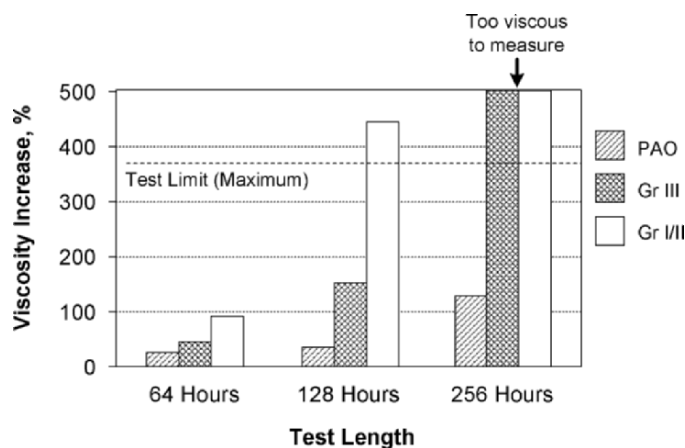


Figure 4. Comparison of viscosity increase in ASTM Sequence IIIE engine test for fully formulated lubricants based on PAO vs. Group III or I/II base stocks¹⁷

- PAO are available in wide viscosity range.

PAO are available from 2 to 100 cSt at 100°C. The high viscosity PAO maintain excellent VI and low pour point (Table 3 and 5), in a manner that is superior to the highest viscosity mineral oil base stock - bright stock. High viscosity PAO are important when blending with low viscosity fluid to formulate high viscosity grade industrial oils. When used to blend with low viscosity mineral oil, the high viscosity PAO also significantly improves the oxidative stability of the blended base stocks compared to using mineral bright stock¹⁵.

- PAOs have high aniline point, indicating low polarity.

Table 5 shows that low viscosity PAO has a higher aniline point than Group I mineral oils, 119°C vs. 100°C (Table 5). A more pronounced difference is observed for high viscosity fluids (>170°C vs. 97°C). The higher aniline points of PAO mean that they are much less polar than Group I oils. Generally, lubricant additives and oil oxidation by-products are highly polar chemical species. As aniline point has relevance to solvency, additives and oil oxidation by-products are not very soluble in PAO alone. As a result, a polar co-base stock, such as ester or alkylaromatic, is usually added to the formulation to improve the solvency of PAO in a finished lubricant. These co-base stocks can also assist other performance features, such as seal compatibility and improved lubricity.

- PAO possess other important properties, depending on application:
 - Compatibility or miscibility with mineral oil at all concentration levels without phase separation or detrimental effects when cross-contamination occurs
 - Hydrolytic stability

- 10% higher thermal conductivity and heat capacity than comparable mineral oil, allowing equipment to run at lower temperature and improve wear performance¹⁸
- Lower traction coefficients than conventional fluids, resulting in better energy efficiency for many industrial oil applications⁶
- PAO are non-greasy and non-comedogenic

In summary, PAO have superior VI, pour point, low-temperature viscosity, volatility, and oxidative stability and are available in a wide viscosity range compared to conventional Group I, II or III mineral oils.

3.1.5 Recent Developments – SpectraSyn Ultra as Next Generation PAO

Following the success with PAO, ExxonMobil Chemical Co. recently introduced a new generation of PAO, trade-named SpectraSyn UltraTM. SpectraSyn UltraTM is produced from the same raw material as PAO, 1-decene, using proprietary catalyst technology^{19, 20}. Table 6 summarizes the properties of commercial SpectraSyn UltraTM products.

Compared to traditional PAOs, SpectraSyn UltraTM PAO have even higher VI, lower pour point and are available in higher viscosity ranges. This unique class of fluid can be used in automotive engine oil and industrial oil formulations to provide advantages in terms of shear stability, viscometrics properties, thickening power and increased lubricant film thickness.

Table 6. Product properties of next generation PAO - SpectraSyn UltraTM

Product	SpectraSyn Ultra TM 150	SpectraSyn Ultra TM 300	SpectraSyn Ultra TM 1000
Kinematic Viscosity @100°C, cSt	150	300	1,000
Kinematic Viscosity @40°C, cSt	1,500	3,100	10,000
Viscosity Index	218	241	307
Pour Point, °C	-33	-27	-18
Flash Point, °C	>265	>265	>265
Specific Gravity @15.6°C/15.6°C	0.850	0.852	0.855

3.1.6 Applications

PAO is the workhorse base stock for most synthetic lubricants. Low viscosity PAO are used in synthetic automotive crankcase and gear lubricants, industrial oils and greases. High viscosity PAO have found great utility in industrial oils and greases.

Synthetic automotive engine oils command the largest volume among synthetic lubricant products. Taking advantage of the many superior properties of PAO base stocks, performance advantages of synthetic engine oils based on PAO over mineral oil-based engine oils are well-documented in scientific and trade literature²¹. They include:

- Improved engine wear protection
- Extended oil drain interval
- Excellent cold starting performance
- Improved fuel economy
- Reduced oil consumption
- Excellent low-temperature fluidity and pumpability
- High temperature oxidation resistance

Many of these performance advantages are directly attributable to the intrinsically superior properties of PAO, such as high VI, low pour point, low low-temperature viscosity, high oxidative stability, low volatility, etc.

The advantage of using synthetic engine oil is further supported by the fact that many automakers use synthetic lubricant as the “factory fill“ lubricant for their high performance cars. For example, in 2003, Mobil 1™ is used as factory-fill lubricant for the Corvette, all Porsches, Mercedes-Benz AMG models, Dodge Viper, Ford Mustang Cobra R and Cadillac XLR²².

PAO blended with mineral oil are also used in many partial synthetic lubricant formulations. In this case, PAO is used as a blending stock to improve the volatility, high or low-temperature viscosity, oxidative stability, etc. of the mineral oil blend.

Synthetic industrial oils and greases, formulated with PAO, have many specific performance and economic advantages over conventional lubricants^{6,21a}. For example, in industrial gear/circulation oils, PAO-based lubricants offer the following documented advantages:

- Energy savings, longer fatigue life and lowered temperatures of operation due to lower traction coefficients
- Wider operating temperature range due to higher VI and better thermal-oxidative stability
- Reduced equipment down-time, reduced maintenance requirements and longer oil life due to the excellent stability of PAO base stock

Because PAO is available in high viscosity grades (up to 100 cSt at 100°C), high ISO grade synthetic industrial oils with improved performance features are more easily formulated. This option is not available for mineral oil-based lubricants.

In compressor oil applications, PAO-based lubricants have advantages due to their better chemical inertness and resistance to chemical attack. Synthetic compressor oils are used in corrosive chemical environments, for example, in sulfuric acid or nitric acid plants. PAO-based lubricants are also used in refrigeration compressor applications due to their excellent low temperature fluidity, lubricity and generally wider operating temperature range.

Other synthetic industrial oil applications with PAO-based lubricants, include gas turbine, wind turbine and food-grade gear lubricants. Synthetic greases based upon PAO are used in industrial equipment, aviation and automotive applications that take advantage of the wide operating

temperature range, high degree of stability and other desirable properties and features offered by PAO base stocks.

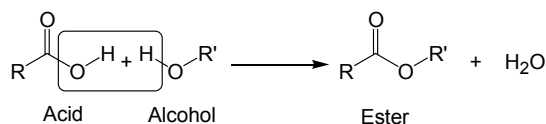
Recently, PAO is finding its way into personal care products such as shampoos, conditioners and skin lotions because it provides emolliency in addition to good skin feel and is non-greasy and non-comedogenic. It is also used in off-shore drilling fluids because of its good lubricity. New applications for PAO are continuously emerging.

3.2 Dibasic, Phthalate and Polyol Esters - Preparation, Properties and Applications

Lard and vegetable oil, both ester-type compounds derived from natural sources, have been used as lubricants throughout human history. After World War II, thousands of synthetic esters were prepared and evaluated as lubricant base stocks for jet engine lubricants.²

3.2.1 General Chemistry and Process

Esters are made by reacting carboxylic acids with alcohols. The elimination of water is shown by the following equation:



The reaction proceeds by heating the mixture to 150°C or higher with or without a catalyst⁹. Catalysts such as p-toluenesulfonic acid or titanium(IV) isopropoxide, are typically used to facilitate reaction rates. The reaction is driven to completion by continuous removal of water from the reaction medium. Sometimes, one component is used in a slight excess to ensure complete conversion. The final product is purified over an adsorbent to remove trace water and acids, both of which are detrimental to base stock quality. Commercially, esters are generally produced by batch processes.

The choice of acid and alcohol determines the ester molecular weights, viscometrics and low temperature properties, volatility, lubricity, as well as the thermal, oxidative and hydrolytic stabilities²³. The structure-property relationships of ester base stocks are well documented in the literature. Compared to PAO and mineral oil, ester fluids have a higher degree of polarity, contributing to the following unique properties:

- Superior additive solvency and sludge dispersancy
- Excellent lubricity
- Excellent biodegradability
- Good thermal stability

Three classes of esters are most often used as synthetic base stocks - dibasic ester, polyol ester and aromatic ester. Some basic properties of these esters are summarized in the Table 7.

Table 7. Basic properties of ester base stocks

Acid	Alcohol	Viscosity, cSt		VI	Pour Point, °C	Wt% Volatility ^(a)	Wt% Biodegradability ^(b)
		100°C	40°C				
Dibasic ester							
Adipate	Iso-C ₁₃ H ₂₇	5.4	27	139	-51	4.8	92
Sebacate	Iso-C ₁₃ H ₂₇	6.7	36.7	141	-52	3.7	80
Polyol ester							
n-C ₈ /C ₁₀	PE ^(c)	5.9	30	145	-4	0.9	100
n-C ₅ /C ₇ /iso-C ₉	PE	5.9	33.7	110	-46	2.2	69
n-C ₈ /C ₁₀	TMP ^(c)	4.5	20.4	137	-43	2.9	96
Iso-C ₉	TMP	7.2	51.7	98	-32	6.7	7
n-C ₉	NPG ^(c)	2.6	8.6	145	-55	31.2	97
Di- and mono-acids	NPG	7.7	40.9	160	-42	--	98
Aromatic Esters							
Phthalate	Iso-C ₁₃ H ₂₇	8.2	80.5	56	-43	2.6	46
Phthalate	Iso-C ₉	5.3	38.5	50	-44	11.7	53
Trimellitate	Iso-C ₁₃ H ₂₇	20.4	305	76	-9	1.6	9
Trimellitate	C ₇ /C ₉	7.3	48.8	108	-45	0.9	69

(a) Noack Volatility : 250°C, 20 mm-H₂O, and one hour with air purge

(b) by CEC-L-33-A-96 test, % degradable in 21 days

(c) PE: pentaerythritol, TMP: trimethylolpropane, NPG: neopentylglycol

3.2.2 Dibasic Esters

Dibasic esters are made from carboxylic diacids and alcohols. Adipic acid (hexanedioic acid) is the most commonly used diacid (Figure 5). Because it is linear, adipic acid is usually combined with branched alcohols, such as 2-ethylhexanol or isotridecanols (C₁₃H₂₇OH) to give esters with balanced VI and low temperature properties (Figure 5). Dibasic ester is most often used as a co-base stock with PAO to improve solvency and seal swell properties of the final lubricants.

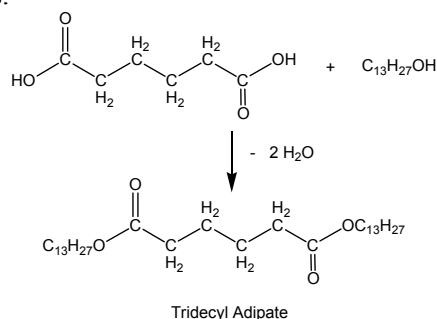


Figure 5. Synthesis of adipate ester

3.2.3 Polyol Esters

The most common polyols used to produce synthetic polyol ester base stocks are pentaerythritol (PE), trimethylolpropane (TMP) and neopentylglycol (NPG), (Figure 6). By carefully choosing the degree of branching and size of the acid functions, polyol esters with excellent viscometric properties - high VI and very low pour points – can be produced (Table 6).

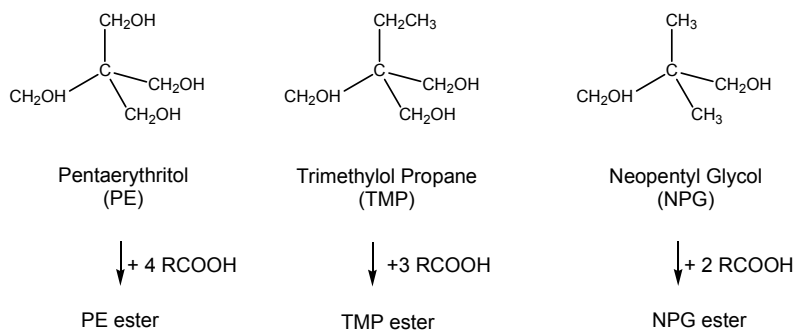


Figure 6. Synthesis of polyol esters

In addition to excellent viscometric properties, polyol esters have the best thermal resistance to cracking. This is because polyols lack β -hydrogen(s) adjacent to the carbonyl oxygen and thus can not undergo the same facile β -H transfer reaction as the dibasic esters (Figure 7). This cracking by β -H transfer leads to two neutral molecules and is a relatively low energy process. Polyol esters can only be cracked by C-O or C-C bond cleavage, leaving two free radicals - a very high-energy process requiring extremely high temperature. Therefore, polyol esters are thermally stable up to 250°.

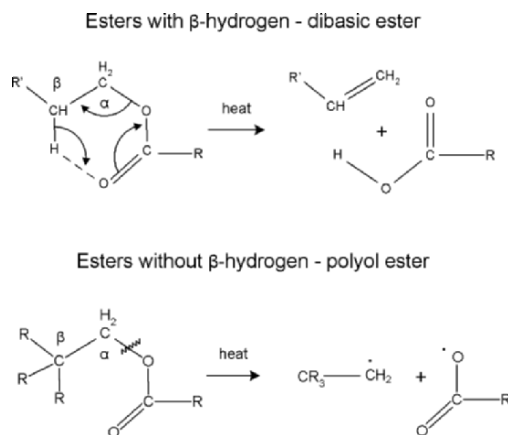


Figure 7. Cracking reaction mechanism for esters - β -H effect

Among the three polyol ester types, the thermal stability ranking is: PE esters > TMP esters > NPG esters.

3.2.4 Aromatic Esters

Phthalic anhydride or trimellitic anhydride are converted into esters by reactions with alcohols as shown in Figure 8. Phthalic anhydride is produced cheaply and in large volume from oxidation of ortho-xylene. The largest use of phthalate esters is in the plasticizer market. Only a small fraction of its production is consumed by the synthetic lubricants market. Phthalate esters generally have superior hydrolytic stability than adipic esters because the ortho di-ester groups are electronically less available and sterically more hindered²⁴. However, they have lower VIs, 50-70, because of their high polarity and the presence of branched alcohol chains. They are used in special industrial oil applications where VI is not a critical parameter. Trimellitate esters are specialty products and relatively expensive. They are of high viscosity and usually are more resistant to oxidation than adipic esters.

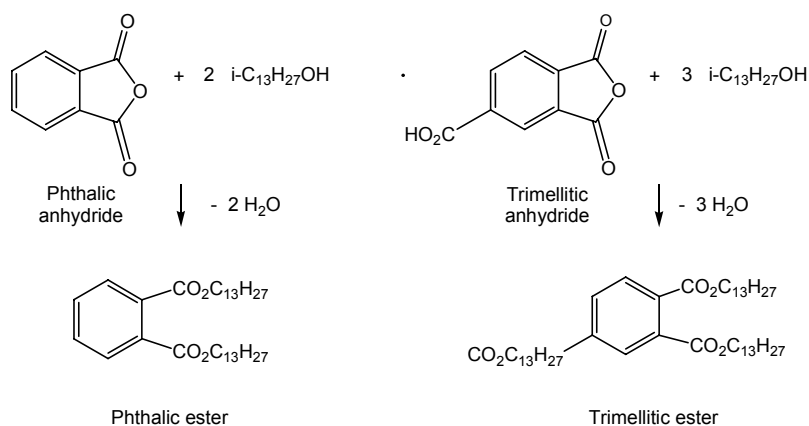


Figure 8. Synthesis of phthalate and trimellitate esters

3.2.5 General Properties and Applications of Ester Fluids

Solvency and dispersancy - Ester fluids are quite polar due to their high oxygen contents. They have high solubility for many commonly used additives. They also have high solubility for the polar acids and sludges generated by oxidation processes during service. This property makes ester based lubricant “clean” compared to hydrocarbon-based lubricants. Typically, low viscosity ester fluids are soluble with non-polar PAO base stocks. These properties make them excellent for use as co-base stocks with PAO in many synthetic automotive and industrial lubricants. Generally, 5 to 25% esters are used with PAO in finished lubricant formulations.

Hydrolytic stability²⁴ - Hydrolysis of esters to give acids and alcohols is a facile reaction and can proceed at elevated temperatures in the presence of water. Hydrolysis of ester generates acid that can be very corrosive to metal components and can catalyze the base stock decomposition process. Therefore, hydrolytic stability of esters is an important issue. Much work has been carried out to improve the hydrolytic stability by varying the composition of acids and alcohols. Generally, esters made from aromatic acids or from more sterically hindered acids, such as 2-alkyl substituted acids or neo-acids, have improved hydrolytic stabilities. Proper branching of the acids protect the carbonyl ester function from the detrimental attack of water. The presence of impurity, such as trace acid or metal, can catalyze the decomposition and hydrolysis of ester. Compared to PAO or alkylaromatic base stocks, ester hydrolysis is always an issue of concern in many lubrication applications.

Volatility - Ester fluids generally have lower volatility compared to PAO and mineral oil of comparable viscosities. A General volatility ranking for base stocks are as follows:

PE ester > TMP ester > dibasic ester > PAO >> Group I or II mineral oil.

Lubricity - Polar ester fluids show mild boundary film protection at lower temperature. At lower temperature, esters interact with the metal surface via polar interaction, forming a chemisorbed surface film, which can provide better lubrication than the less polar mineral oil or non-polar PAO. When esters decompose, they produce acids and alcohols. Higher molecular weight acids can bind with the metal surfaces to form a film that can offer some degree of wear protection and friction reduction. However, none of these interactions are strong enough to persist when surface or oil temperature rises much above 100°C. At higher temperature, significant wear protection can only be achieved by the use of anti-wear or extreme-pressure (EP) additives. A drawback for the ester high polarity is that esters can compete with metal surface for polar additives, resulting in less efficient usage of anti-wear and EP additives. Therefore, in formulations using esters, it is important to choose the proper additives and concentration levels to obtain the full benefit of the lubricity from both the additives and esters.

Biodegradability - By carefully choosing the molecular compositions, esters of excellent biodegradability can be produced. Generally, esters from more linear acids and alcohols have better biodegradability.

Applications²⁵ - Esters, both dibasic and polyol esters, are used as co-base stocks with PAO or other hydrocarbon base stocks in synthetic automotive engine lubricants and industrial lubricants. Polyol esters are used in aircraft turbine oils due to their excellent thermal and oxidative stabilities, good lubricity, high VI and excellent low temperature properties (<-40°C)^{21a}. Esters are also used in synthetic compressor oils for ozone-friendly refrigeration units. Because of their high biodegradability and low toxicity, esters are often the base oils of choice for many environmentally-aware

VIs, pour points, water solubilities and oil-compatibilities are produced by choosing the proper initiators, monomers, reaction conditions and post treatments. The reaction is highly exothermic (22.6 kcal/mole) and heat removal is important to avoid side-reactions or broadening of the product molecular weight distribution.

3.3.2 Product Properties

Table 8 summarizes the typical lubricant properties of selected PAG produced from EO, PO and BO with several different initiators.²⁸

Table 8. Lube properties of PAG fluids from EO, PO and BO with different initiator

	AO Type	End Group	Avg. MW	KV _{100°C} cSt	KV _{40°C} cSt	VI	Pour Point, °C	Density, g/cm ³	Solubility in oil	Solubility in water
E300	EO	OH/OH	300	5.9	36	118	-10	1.125	i	s
E600	EO	OH/OH	600	11.0	72	154	22	1.126	I	s
P425	PO	OH/OH	425	4.6	33	26	-45	1.007	--	--
P1200	PO	OH/OH	1200	13.5	91	161	-40	1.007	--	i
PB200	PO	Bu/OH	910	8.3	44	180	-48	0.9831	--	i
EP530	EO/PO	OH/OH	2000	25	168	192	-32	1.017	--	--
EPB100	EO/PO	Bu/OH	--	4.8	101	174	-57	1.0127	--	s
EPB260	EO/PO	Bu/OH	--	11.0	56.1	210	-37	1.0359	--	s
B100-500	BO	OH/OH	500	5.1	44.3	3	-30	0.975	s	s
B100-2000	BO	OH/OH	2000	24.7	234.7	142	-26	0.970	s	i
1500 MW poly BO Mono-ol	BO	Bu/OH	1500	15.8	117.1	153	-30	0.961	s	i

EO-based fluids are typically waxy and have poor low temperature properties. They have high water miscibility and are typically used to formulate water-based lubricants, especially fire-resistant hydraulic oil. PO-based fluids are excellent lubricant base stocks with high VI and low pour point. They have lower solubility in water than EO-based fluids but are not oil miscible.

EO/PO-based fluids have a better combination of VI and low pour points than PO-based products. They are used as base stocks in industrial circulation/gear oils.

BO-based PAG have improved oil solubility and are not water-soluble.

PAG generally have excellent lubricity and low friction coefficients compared to mineral oil as shown in Table 9. These properties result from the facile surface chemisorption of the oxygenate functions or through hydrogen bonding of the terminal OH groups with the metal surface.

Other unique properties for PAG include:

- superior solvency - they dissolve additives, decomposition products and sludges
- non-varnishing and low ash - they leave little or no residue or carbon black upon decomposition

Table 9. Lubricating properties of selected PAG fluids²⁸

Fluid Type	Mol. weight	V100°C ,cSt	V40°C cSt	VI	Pour point, °C	Four ball wear scar, mm (a)	Four ball seizure load, kg (a)	Friction coefficient (b)	Soluble in (c)
EO/PO	500	4.6	19	161	-46	0.53	120-140	0.15	water
EO/PO	1300	15	76	218	-42	0.44	180-200	0.11	water
PO	700	6	27	179	-44	0.53	160-180	0.19	oil (d)
PO	1300	14	73	193	-35	0.57	120-140	0.12	none

(a) by DIN 51350 method

(b) determined by oscillation of a steel ball on a steel disc at 30°C under a load of 200 N

(c) determined by mixing equal proportions of water and PAG or oil and PAG.

(d) partially soluble in oi

3.3.3 Application

The major use of PAG is in the industrial oil area²⁹:

- Fire resistant hydraulic fluids. Water-soluble PAG are fire resistant, low toxicity and have excellent lubricity and anti-wear properties.
- Textile oils. PAG are non-varnishing, non-staining and can be washed away with water.
- Compressor and refrigeration oils. Low solubility of many industrial gases, such as natural gas and ethylene, makes PAG suitable for gas compressor applications. PAG are compatible with new refrigerants (HFC-143a) and have excellent anti-wear properties.
- Metal working fluids. PAG are non-varnishing, have excellent lubricity and anti-wear properties.
- Circulation/bearing/gear oil. Low friction coefficients and traction properties of PAG lead to lower operating temperature and energy consumption. They have good anti-wear properties and are non-varnishing.

3.4 Other Synthetic Base Stocks

Polyisobutylene (PIB) fluids are produced by the oligomerization of isobutylene in a mixed C₄ stream over a BF₃ or AlCl₃ catalyst. PIB are seldom used by themselves. They are typically used as blend stocks or as additives to increase lubricant viscosity. Table 10 summarizes the typical properties of selected PIB fluids³⁰. The VI and pour points of PIB are comparable to those of conventional mineral oil. PIB usually have a lower flash point and decompose easily into monomer at 200°C and higher. The advantages of PIB are their high compatibility with most synthetic or mineral base stocks and their relatively low cost compared to other synthetic base stocks.

Table 10. Typical physical properties of PIB available from BP Chemical Co.

	H-25	H-50	H-100	H-300	H-1500
Kinematic Viscosity @100°C, cSt	50	100	200	605	3000
Viscosity Index	87	98	121	173	250
Pour Point, °C	-23	-13	-7	3	18
Bromine Number (?)	27	20	16.5	12	8
Flash Point, °C (a)	171	193	232	274	307
Molecular Weight (b)	635	800	910	1300	2200

(a) by Cleveland open cup ASTM D92 method.

(b) by gel permeation chromatography.

Alkylbenzenes and alkylnaphthalenes are produced by the alkylation of benzene or naphthalene with olefins using Friedel-Crafts alkylation catalysts³¹. Their typical properties are summarized in Table 11. One unique feature of these alkylaromatic fluids is their very low pour points. Alkylbenzenes are often mentioned in the patent literature as components for CFC or HCFC refrigeration compressor oil. Alkylnaphthalenes are used in synthetic automotive engine oil, rotary compressor oils, and other industrial oils.

Table 11. Properties of alkylbenzene and alkylnaphthalenes base stocks

Fluid type	Di-alkylbenzenes	Di-alkylbenzenes	Alkylnaphthalenes
Commercial source	V-9050 from Vista Chem. Co.	Zero 150 from Chevron	Synesstic™ 5 from ExxonMobil Chem.
Kinematic Viscosity @100°C, cSt	4.3	4.4	4.7
Kinematic Viscosity @40°C, cSt	22.0	33.5	28.6
VI	100	25	74
Pour Point, °C	-60	-40	-39
Flash Point, °C	215	170	222
Aniline Point, °C	78	--	33

Phosphate esters are produced from phosphorus oxychloride with various alcohols or phenols, or combinations of these hydroxyl compounds³². These fluids generally have good thermal and oxidative stabilities and fire-resistancy. However, because of their high polarity, poor VI-pour point balance, facile hydrolysis³³ and inferior elastomer and paint compatibility, their use in general lubrication is limited. The major use for phosphate esters is in fire-resistant hydraulic oils.

4. CONCLUSION

Synthetic lubricants have significantly raised the performance level of automotive and industrial lubricants with the help of high-quality PAO base stocks and tailored high-performance additive technologies. Equipment builders, industrial users and general consumers have taken advantages of the enhanced performance benefits afforded by synthetic lubricants - reduced

maintenance and waste, lower emissions and pollution, higher reliability and efficiency, etc. As a result, in the last ten years, synthetic lubricants have enjoyed yearly growth rates of 5-10%, a range considerably higher than for conventional lubricants³⁴. This growth rate has occurred despite the higher initial costs of synthetic products. The higher initial costs have been economically offset by the extended life and performance benefits afforded by synthetic lubricants.

This trend is expected to continue in the finished lubricants market. In the short-term, the growth for some PAO-based synthetic lubricants may slow temporarily due to new competition from hydroprocessed base stocks³⁵. However, high-performance synthetic base stocks and finished lubricants should continue to prove their enhanced and well-documented values as further demands on lubricant performance grow. The knowledgeable user, who treats the lubricant as an active machine component and understands the enhanced performance and associated economic benefits, will continue to demand greater efficiency, reduced maintenance, lower emissions and longer service life, etc, offered by high-quality synthetic lubricants. These factors should increase market value and continue market growth for advanced synthetic lubricants. To meet this demand, the leaders of the lubricant industry will need to respond by developing and marketing next-generation, high performance base stocks and products. ExxonMobil's SpectraSyn UltraTM and Mobil 1TM with SuperSynTM-Antiwear technology are current examples of this leadership.

5. ACKNOWLEDGEMENT

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