

Exploring the functionality of oxygen-rich Secondary Polyol Ester™ base oils

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Introduction

Synthetic esters represent one of the most versatile and widely used classes of base oils in the lubrication industry. For over 80 years, they have delivered reliable solutions across automotive, industrial, and marine sectors. Over the decades, a diverse array of synthetic ester families has been developed, including mono-carboxylic acid esters, dicarboxylic acid esters, polyol esters, and trimellitate esters, among others. As we look to the future, synthetic esters will continue to address complex tribological challenges that other base fluids are unable to meet.

Despite their numerous functionalities and performance advantages, including favourable environmental attributes, the introduction of new synthetic ester families remains rare. This is largely due to the substantial investment required to bring a new base oil technology to market. The costs associated with research and development, application development, regulatory approval, marketing, and manufacturing scale-up are significant factors in the commercialisation process. Before investing in an innovative product development program, it is necessary to assess the technical and commercial risks, as well as the industry's willingness to move away

from petroleum oils, which have been the dominant base oil choice for lubricants over the past century.



Industry Mega-Changes & Lubricant Innovation

Technology Revolution	Implications for Lubricant Technology Development
<input type="checkbox"/> Robotics	✓ Advanced base stocks
<input type="checkbox"/> Advanced computing	✓ Superior heat management versus hydrocarbon oils
<input type="checkbox"/> Digitization	✓ Increased volumetric heat capacities and thermal conductivities
<input type="checkbox"/> Electrification (EVs)	✓ More thermo-oxidatively stable lubricants
<input type="checkbox"/> Higher industrial productivity	✓ Safer lubricants (fire resistant, food safety)



Energy Transition	Implications for Lubricant Technology Development
<input type="checkbox"/> UN climate change policy	✓ Energy efficient lubricants (friction control, fuel economy)
<input type="checkbox"/> EU Green Deal	✓ Lubricants from alternative feedstocks (oleochemical feedstocks)
<input type="checkbox"/> Circular economies	✓ Longer life fluids (less waste)
<input type="checkbox"/> Decarbonization	✓ Recycling/reconditioning
<input type="checkbox"/> Sustainable development	✓ LCAs/ Product carbon footprint

Figure 1: Macro-trends influencing base oil development

Figure 1 illustrates several key macro-trends within our industry that are currently shaping lubricant product development. A significant political movement across most regions is driving a major energy transition, influenced by frameworks such as UN climate change policies, the EU Green Deal, the push for circular economies, decarbonisation, and sustainable development. Alongside this, a technological revolution, often referred to as 'Industry 4.0,' is unfolding, characterised by advances in electrification, digitisation, robotics, and advanced computing.

Petroleum-based lubricants and fluids are increasingly challenged to meet the stricter performance and environmental specifications set by OEMs. As a result, our industry faces a growing demand for innovation and the development of advanced lubricants that are more energy-efficient, ideally sourced from alternative feedstocks, and offer superior heat management and stability.

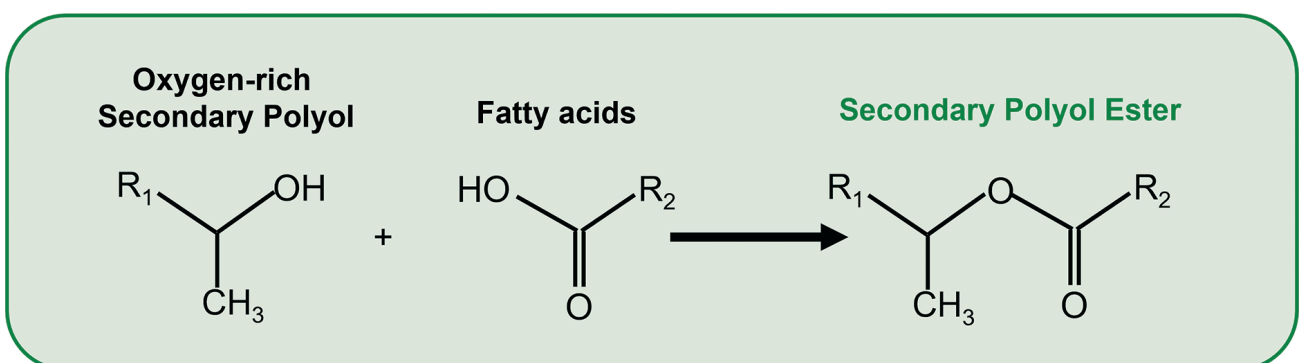
To address these emerging trends, a new class of synthetic ester, known as Secondary Polyol Ester™ base oils, has been developed. These esters are distinguished from conventional esters by the inclusion of a significant amount of oxygen in the form of ether bonds within their structure, which introduces new functionalities and qualities to the synthetic ester family. This article examines their innovative aspects and highlights some of the functionalities that can address emerging tribology challenges.

Secondary Polyol Ester™ Technology

Secondary Polyol Ester (SPE®) base oils are designed for both high performance and sustainability. They are produced by reacting a proprietary polyol with fatty acids derived from either oleochemical or petrochemical feed stocks. The esterification process occurs at a secondary hydroxyl group of the polyol, resulting in novel, "oxygen-rich" SPE base oils (as depicted in Figure 2).

The high oxygen content, present as ether bonds within the ester molecule, significantly impacts both the physical and functional performance of these unique base oils (as shown in Figure 3). This results in "hybrid functionality," where SPE base oils combine many of the functional advantages of PAGs with the environmental characteristics of esters. For instance, they can achieve higher viscosity indices, lower aniline points (indicating high polarity), and low traction coefficients. Additionally,

Designing the SPE® molecule with high levels of oxygen imparts new functionality to the performance of synthetic esters



Structural Design Features

- Deposit control
- Hydrolytic stability
- Low heats of combustion
- Load bearing
- Friction control
- Low temp. performance

Structural Design Features

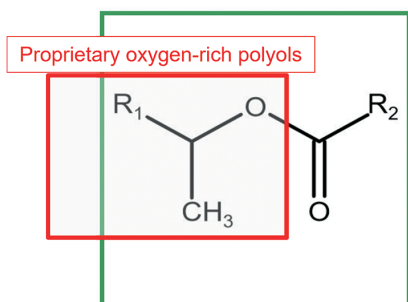
- High bio-carbon content
- Viscosity control
- Antiwear
- Oxidative stability (saturated)

Performance Features

- Varnish control
- High volumetric heat capacity
- Fast air release
- Oxidation stability
- Hydrolytic stability
- Low friction
- Low temperature stability
- Readily biodegradable

Figure 2: Building functionality and performance through esterification

Novel Secondary Polyol Ester™ Technology



ISOVG 32 to 460

Hybrid structures: Functional performance of PAGs and environmental performance of esters

General design rules when increasing oxygen content in esters

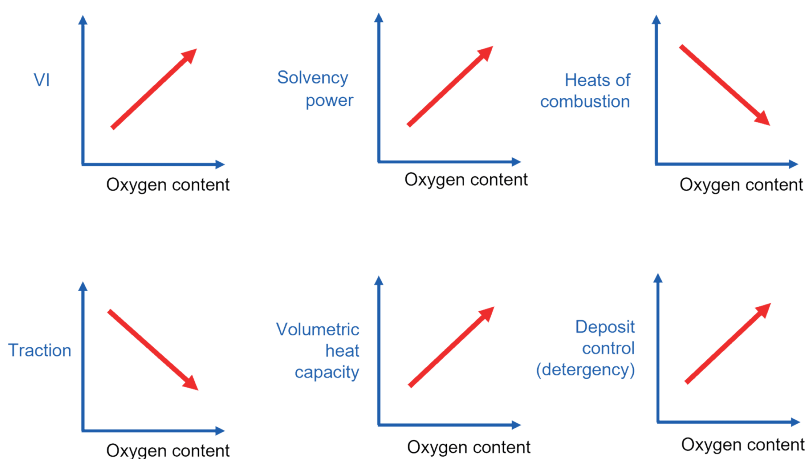


Figure 3: Influence of oxygen content on ester functionality

they possess favourable thermo-physical properties such as higher volumetric heat capacities and low heats of combustion, which are distinctive features.

Secondary Polyol Ester™ Base Oils (Gen 1)

S = Saturated
U = Unsaturated

	32S	46S	46U	68S	68U	100S
Kinematic viscosity at 40°C, mm ² /sec	29.5	44.2	53.6	69.4	66.9	96.9
Kinematic viscosity at 100°C, mm ² /sec	6.1	8.6	10.7	12.1	12.9	15.5
Viscosity Index	162	177	196	173	198	170
Pour point, °C	-60	-42	-30	-33	-39	-36
Density at 40°C, g/ml	0.97	0.96	0.97	0.95	0.95	0.93
Fire point, °C	262	264	324	276	322	280
Noack volatility, %	14.2	13.3	0.8	6.7	1.0	4.5
Biodegradation* (OECD301B), %	>80	>80	>80	>80	>80	>80
Bio-based carbon (%)	62.5	50	76	59	65.5	65.5

Typical values

Figure 4: Physical property data for lower viscosity SPE base oils

Secondary Polyol Ester™ Base Oils (Gen 2)

C = Complex
S = Saturated

	100CS	150CS	220CS	320CS	460CS
Kinematic viscosity at 40°C, mm ² /sec	99.5	150	231	315	445
Kinematic viscosity at 100°C, mm ² /sec	16.9	24.6	35.0	46.2	62
Viscosity Index	185	196	200	208	213
Pour point, °C	-18	-18	-18	-21	-21
Density at 40°C, g/ml	0.97	0.97	0.97	0.97	0.98
Flash point, °C	276	242	244	248	262
Aniline point, °C	<-10	<-10	<-10	<-10	<-10
Biodegradation* (OECD301B), %	>80	>80	>80	>80	>80
Bio-based carbon (%)	57	54	54	53	50

Typical Values

Figure 5: Physical property data for Complex SPE base oils

The fundamental SPE® structure is highly adaptable, allowing for the design of a wide range of molecular

structures tailored to address current and future tribology challenges. Figures 4 and 5 provide physical property data for SPE base oils across the viscosity range ISO-32 to 460.

Functionalities of SPE Base Oils

In-Built Detergency

Natural and synthetic esters are more polar than hydrocarbon oils, which is reflected in their lower aniline points. This polarity can be further enhanced by incorporating a high density of ether bonds into their structure, resulting in even lower aniline points for these oxygen-rich molecules. The high oxygen content also provides these molecules with inherent detergency properties. When using synthetic lubricants formulated with SPE base oils as the primary base oil, equipment can benefit from superior cleanliness and reliability. This is particularly relevant for applications such as hydraulic fluids, turbine oils, and compressor fluids, where high levels of deposits and varnish can form when petroleum oils degrade through oxidation.

Alternatively, SPE molecules can be used as deposit control additives at low treat levels in formulations

where a hydrocarbon oil is the primary base oil. Their high polarity and solubility in hydrocarbon base oils can improve the solvency power of API Group II-IV base oils, which typically have high aniline points (low polarity). Using SPE base oils as additives at low treat levels can help control deposits that form as hydrocarbon base oils age, thus preventing the dangerous buildup of varnish in equipment. This, in turn, can enhance equipment reliability, reduce downtime, and extend lubricant life.

A Differential Scanning Calorimetry (DSC) experiment was conducted to demonstrate the cleanliness functionality of SPE base oils. In this test, an API Group III base oil, a polyalphaolefin (Group IV), an adipate ester (Group V), and two SPE base oils (32S and 46S) were aged by heating the base oils at a rate of 10°C per minute up to 400°C in an air atmosphere. Figure 6 illustrates the residue formation after the test, which is significantly lower for the SPE base oils, highlighting their superior cleanliness properties.

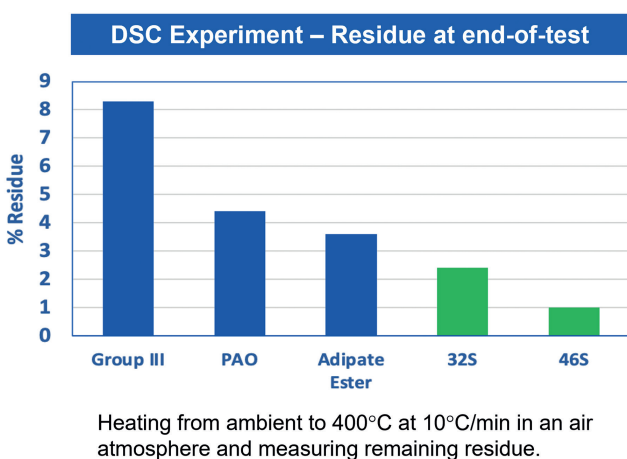


Figure 6: Thermo-oxidative degradation performance of base oils

Volumetric Heat Capacities

Thermal management in modern automotive and industrial equipment has become an increasingly important area of focus, as many lubricants are now subjected to more intense thermal stresses. Researchers are developing a growing body of knowledge on the

thermo-physical properties of modern lubricants, such as specific heat capacity, thermal conductivity, and, in some applications, electrical conductivity. This is particularly relevant with the rise of electric vehicle fluids.

The specific heat capacity of a substance refers to the amount of heat required to raise the temperature of one unit of mass by one degree. Since most equipment operates with a specific volume of fluid, understanding a fluid's volumetric heat capacity is even more critical. Volumetric heat capacity, which indicates the amount of heat needed to raise a unit volume of a substance by one degree, is calculated by multiplying the specific heat capacity of the lubricant by its density. The high oxygen content in SPE ester molecules results in higher volumetric heat capacities compared to many conventional base oils.

	ISO Viscosity Grade	Density at 40°C (g/ml)	Specific heat capacity at 40°C, J/g/K	Volumetric heat capacity (J/cm ³ /K)
TMP-Trioleate**	46	0.903	2.03	1.83
PAO-6**	32	0.811	2.33	1.88
46S (Saturated)	46	0.960	2.10	2.02*
68U (Unsaturated)	68	0.950	2.17	2.06*

* Measured using ASTM D7896-19
 ** Thermochemica Acta 703, (2021) 178994

Figure 7: Volumetric heat capacity of base oils

Figure 7 demonstrates the superior volumetric heat capacity of two SPE base oils (46S and 68U) compared to a polyalphaolefin base oil and a traditional synthetic ester (TMP trioleate). The SPE base oils show values up to 12% higher. This enhanced heat management capability could lead to formulations that result in slower oxidation rates and equipment operating at cooler temperatures.

Hydrolytic Stability

Synthetic esters offer a broad range of functionalities, but a practical concern in formulating new lubricants with certain esters is their susceptibility to hydrolytic instability. While some esters are easily prone to hydrolysis, others have been meticulously designed to minimise this risk. For example, selecting branched

acids as precursors is known to enhance hydrolytic stability compared to using linear acids. Additionally, during the manufacturing process and post-treatment, the residual free acid content can be minimised or eliminated to optimise stability, as free acid can catalyse the hydrolysis of esters.

SPE® base oils are specifically designed from a highly branched proprietary polyol, which provides steric hindrance around the ester groups, significantly improving their stability compared to many other esters. Figure 8 presents data from the ASTM D2619 (Beverage Bottle) test, where four saturated SPE base oils were evaluated. In this test, 25% water and a copper catalyst were added to the fluid, which was then aged for 48 hours at 93°C. The acid number changes observed were minimal, with increases of less than 0.5 mgKOH/g, indicating good stability under these conditions.

Hydrolytic Stability using ASTM D2619

	32S	46S	68S	100S
Acid number change, mgKOH/g	0.28	0.13	0.2	0.46
Copper appearance	1B	1B	1B	1B
Copper loss (mg/cm ²)	-0.083	-0.008	-0.025	-0.033
Kin. viscosity change (%)	-3.3	-2.1	-0.2	-1.8
Insolubles (%)	0.02	0.02	0.03	0.02

Figure 8: Hydrolytic stability of saturated SPE base oils

Fire Resistance

Synthetic esters are commonly used as base oils in fire-resistant hydraulic fluids, with examples including trimethylolpropane (TMP) trioleate and neo-pentyl glycol dioleate. To evaluate a fluid's potential fire resistance, factors such as auto-ignition temperature, fire point, volatility, and heat of combustion are considered. Unsaturated SPE base oils (46U and 68U) exhibit notably high fire points, exceeding 320°C (as shown in Figure 4), and have low volatilities. Additionally, the high oxygen content in their molecular structure results in lower heats of combustion compared to petroleum oils and other synthetic esters.

These properties, combined with their high viscosity indices and excellent low-temperature performance, make SPE base oils an outstanding choice for formulating fire-resistant fluids, such as HFDU fire-resistant hydraulic fluids, which are used in demanding applications like steel and aluminum processing and the mining industry.

Environmental Accreditations

SPE base oils are specifically engineered to be highly biodegradable. They are produced from feedstocks with a high bio-carbon content and are both non-toxic and non-bioaccumulative. These base oils are approved and listed on the EU Lubricant Substance Classification (LuSC) list and have earned the USDA Biobased Product label. These certifications make them an excellent choice for creating environmentally friendly lubricants. Additionally, each base oil has NSF HX-1 certification, allowing them to be used in food-grade lubricants where incidental food contact may occur.

Formulating with SPE Base Oils - Response of Antioxidants

Formulating lubricants requires knowledge of additives that work both in the bulk phase (such as antioxidants and viscosity index improvers) and on surfaces (such as corrosion inhibitors and anti-wear agents). When assessing the performance of additives in new base oils, it is often essential to first understand how conventional antioxidants respond in these base oils.

When evaluating the oxidation performance of lubricants, bulk fluid oxidation testing is often preferred. Various tests are available, such as ASTM D943 (Oxidation characteristics of inhibited mineral oils), ASTM D2893 (Oxidation Characteristics of Extreme Pressure Oils), and ASTM D2272 (Oxidation stability of steam turbine oils by Rotating Pressure Vessel Oxidation Test), which may require several months to complete a test program. An alternative, faster method is thin-film oxidation testing using

Differential Scanning Calorimetry (DSC), which provides insights into how base oils respond to antioxidants by studying thermal transitions as materials are heated.

In this study, the effectiveness of two aminic antioxidants and two hindered phenolic antioxidants, known as primary antioxidants, was evaluated at a 1% by weight concentration, as single antioxidants in saturated and unsaturated SPE™ base oils. The performance of these antioxidants in SPE base oils was compared to TMP trioleate (as shown in Figure 9.) The SPE base oils demonstrated a strong positive response to all four antioxidants. Aminic Antioxidant A exhibited the most notable improvement, with the onset temperature of degradation rising by up to 56°C compared to the virgin base oil. Aminic Antioxidant B and Hindered Phenolic Antioxidants C and D also showed significant increases in onset temperature, ranging from 24°C to 35°C.

In contrast, the aminic antioxidants exhibited a minimal effect in TMP trioleate, with only a 15°C increase, and a moderate 21°C to 30°C improvement for the hindered phenolic antioxidants. Thus, either conventional aminic or hindered phenolic antioxidants are effective choices for formulating lubricants with SPE base oils.

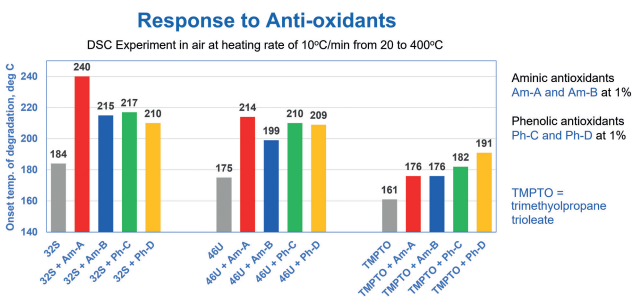


Figure 9: Base oil response to antioxidants using DSC

SPE Base Oils for Bio-hydraulic Fluids

Modern hydraulic equipment often features higher power densities and smaller reservoirs (see Figure 10), which subject the hydraulic oil to significant thermal

stress. Traditional petroleum-based hydraulic oils are vulnerable to oxidative and thermal degradation, leading to deposit formation and varnish. This varnish can severely affect equipment reliability.

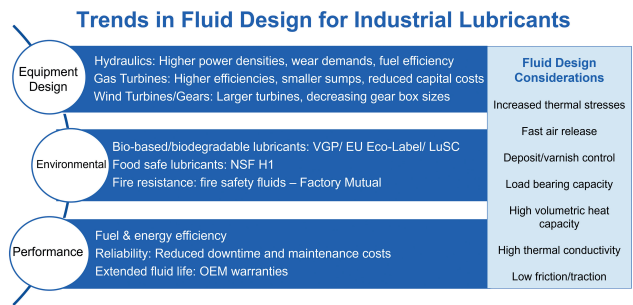


Figure 10: Trends in industrial equipment and lubricant design

SPE base oils, however, are well-suited to manage thermal stresses due to their high volumetric heat capacities and oxidation stability. Additionally, their inherent detergency helps reduce the risk of varnish formation. Coupled with their high biodegradability, non-bioaccumulation, and non-toxicity, SPE base oils are an excellent choice for formulating environmentally friendly bio-hydraulic fluids.

Performance a Bio-Hydraulic Fluid using 46S compared to ISO-15380 specification

Property	Method	Typical Limits	Bio-HF (46S)
Kin. viscosity at 40°C, (cSt)	ASTM D445	Report	45.1
Kin. viscosity at 100°C, (cSt)	ASTM D445	Report	8.7
Kin. viscosity at 0°C, (cSt)	ASTM D445	780 max	402
Viscosity Index	ASTM D2270	Report	174
Acid number (mg KOH/g)	ASTM D974	Report	0.18
Air release at 50°C (min)	ASTM D3427	7 max	0.1
Copper corrosion (3h at 100°C)	ASTM D130	2 max	1A
Demulsibility at 54°C (min)	ASTM D1401	Report	40-37-03 (25)
Foam sequence I (mL)	ASTM D892	150-0 max	0-0
Foam sequence II (mL)		80-0 max	0-0
Foam sequence III (mL)		150-0 max	0-0
TAN change (mg KOH/g)	ASTM D2619	n/a	0.09
Water acidity (mg KOH/g)		4 max	2.30
Cu weight loss (mg/cm ²)		0.2 max	-0.1
Cu rating		Report	2C
Rust (Salt)	ASTM D665B	Pass	Pass
Dry TOST Lifetime (h)	ASTM D943 (dry)	Report	1344 (ongoing testing)

Figure 11: Performance of a Bio-hydraulic Fluid using VBASE 46S

Formulation	Weight %
46S	98.746
EL Additive Pack*	1.25
Foam control additive	0.004

*EL Additive Pack is an ashless package containing antioxidants, anti-wear and corrosion inhibitors

Figure 11 illustrates the performance of an ISOVG-46 bio-hydraulic fluid formulated with an SPE base oil and an additive package derived from environmentally friendly components, with an additive treat level of 1.45% by weight. This formulation was developed to meet the ISO-15380 standard for environmentally acceptable hydraulic fluids (HEES). The fluid demonstrated a high viscosity index, excellent corrosion resistance to both ferrous and yellow metals, good demulsibility, and outstanding foam control. Notably, it achieved an air release time of 0.1 minutes, which is exceptionally fast. This is significant as smaller equipment reservoirs challenge the air release performance of hydraulic fluids. Rapid air release without foaming is crucial, as entrained air can impair fluid compressibility and cause cavitation. Research indicates that formulations using polar SPE base oils generally achieve quick air release times.

Assessment of Elastomer Compatibility per ISO-15380 Specification (HEES)

Elastomer	Property	ISO 15380 Specification	Bio-HF (46S)
HNBR, 1008h, 80°C	Hardness Change	-10 to +10	-1
	Volume Change (%)	-3 to +10	1
	Tensile Strength Change (%)	30 max	1
	Elongation Change (%)	30 max	6
FKM, 1008h, 80°C	Hardness Change	-10 to +10	-2
	Volume Change (%)	-3 to +10	1
	Tensile Strength Change (%)	30 max	-6
	Elongation Change (%)	30 max	9
NBR1, 1008h, 80°C	Hardness Change	-10 to +10	-5
	Volume Change (%)	-3 to +10	7
	Tensile Strength Change (%)	30 max	-3
	Elongation Change (%)	30 max	1

Formulation	Weight %
46S	98.746
EL Additive Pack	1.25
Foam control additive	0.004

Figure 12: Elastomer compatibility of a Bio-Hydraulic Fluid using VBASE 46S

The bio-hydraulic fluid also exhibited good hydrolytic stability, with only a minor increase in acid value following the ASTM D2619 test. Compatibility with elastomers is another challenge for hydraulic fluids made from polar base oils such as esters and PAGs. However, the elastomer test results (see Figure 12) for nitrile rubber (NBR), hydrogenated nitrile rubber (HNBR), and fluoroelastomers (FKM) were excellent

and met the ISO 15380 specification. Field trials are planned to further explore and validate this innovative technology.

Conclusions

Secondary Polyol Ester™ (SPE®) base oils are engineered for both performance and sustainability. Their molecular structure, which includes high levels of oxygen, imparts unique properties that enhance heat management in lubricants due to their superior thermo-physical characteristics. Additionally, their inherent detergency and cleanliness capabilities help reduce deposit formation in equipment. Combined with their excellent environmental performance, these features make SPE base oils ideal for developing innovative, sustainable lubricants that address the challenges of tomorrow's lubricant market.

References

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