

Novel hybrid esters: Base oils designed for sustainability

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Environmental Social Governance (ESG) is now a critical component of the strategies of many organisations. Customers, communities, regulators, and investors are seeking assurance that sustainable practices addressing issues such as climate change and energy conservation are being adopted. In our lubricant industry, significant innovation in new lubricant product development continues to evolve as can be seen with products that offer superior energy and fuel efficiency than their predecessors or indeed are safer for the environment. As organisations work to meet the expectations of ESG including Societal Development Goals (SDG), the development of lubricants continues to evolve to meet sustainability goals without sacrificing performance. Newly developed base oils that were designed from the outset for sustainability are meeting the requirements for both performance and sustainability.

Innovation in the development of bio-lubricants and environmentally-acceptable lubricants has seen the evolution and adoption of new products for at least the past 30 years. Natural esters and synthetic esters have often been the preferred choice of base

oil when formulating bio-lubricants. Natural esters such as rapeseed oil, soybean oil and sunflower oil offer very high levels of biodegradability and have found use in equipment where thermal stresses are low. Chemically they are triglycerides, and their performance is largely determined by the type of acid fraction within their backbone and the levels of oleic, linoleic and linolenic acids in each fraction(1). Synthetic esters are often preferred when the thermal stress on the lubricant is higher, or the lubricant is used in extreme cold climates. Many synthetic esters are derived from petrochemical feedstocks but some are derived from bio- or oleochemical feedstocks(2). Bio-based products are made of renewable carbons and are described in terms of their 'Percent Renewable Carbon Content' as measured using carbon dating techniques. Historically, the focus in the EU has been on biodegradation; however, with the push towards more sustainable solutions, the biobased content or renewability of lubricants are gaining emphasis. However, as the UN Sustainable Development Goals focus on protecting water quality and air quality with reduced carbon footprint, both of these focus points are being brought into harmony.

Over the past 80 years, the versatility of synthetic ester chemistry has led to the adoption of many classes of esters in the lubricant industry and include, for example, mono- and di-carboxylic acid esters, neo-polyol esters, complex esters and aromatic esters(2). The past 10-15 years has seen the development and advancement of estolides and high-oleic containing vegetable oils leading to the emergence of new bio-lubricant products.

Polyalkylene glycols (PAG) are also an option when formulating bio-lubricants. Many PAGs below a molecular weight of about 1500g/mol. (approx. ISO VG-68) offer high levels of biodegradability. It is known that they perform well in equipment when the thermal stresses are high. A significant advantage of PAGs versus many esters is their superior hydrolytic stability making them a preferred choice where water ingress into the lubricant is a concern. However, most PAGs today are derived from petrochemical feedstocks such as ethylene oxide, 1,2-propylene oxide and 1,2-butylene oxide(3), and this restricts their use where environmental regulations stipulate a high renewable carbon content. PAGs with much higher molecular weights often have low levels of biodegradability. Table 1 describes typical environmental aspects of many classes of base fluids that historically are used in formulating bio-lubricants.

	Biodegradability, % (OECD 301B)	Bio-based Content
Vegetable oils	90-100	High
Di-carboxylic acid esters	10-80	Low to High ^(a)
Linear neo-polyol esters	50-90	Low to High ^(a)
Branched neo-polyol esters	5-40	Low to High ^(a)
Complex polyol esters	10-90	Low to High ^(a)
Aromatic esters	0-40	Low
PAGs	20-80	Low
Mineral oils	0-20	Low

^(a) Dependent on the source of acids (petrochemical or oleochemical).

Table 1: Typical biodegradability ranges and bio-based (renewable carbon) content.

A recent approach to developing higher viscosity base oils that maintain biodegradability without sacrificing

performance is to build the molecule using lower molecular weight blocks that can biodegrade in less than 28 days and linking them together with ester bonds. This “Designed for Sustainability” approach has led to the development of hybrid-esters that combine the functional performance advantages of both synthetic esters and PAGs together with the environmental profiles of natural esters. Starting with materials that are known to be non-toxic, non-bioaccumulating, and biodegradable and linking them together with a secondary ester bond that is significantly more stable to hydrolysis than a traditional neo-polyol ester (NPE) allows for the first base oils truly designed for a total lifecycle(4). The new family of hybrid-base oils developed using this approach are being described as secondary polyol esters™ (SPE). Below are some of their functional performance properties as base oils for environmentally acceptable lubricants. Unique features are highlighted which may provide advantages for the creation of future generations of bio-lubricants. More recently, formulations have been developed containing SPEs to demonstrate their suitability for use in equipment and especially in equipment operating in environmentally sensitive areas.

Chemistry of SPEs

The versatility of ester chemistry is well known. For example, top-tier esters such as saturated neo-polyol esters are derived by reacting polyols such neo-pentyl glycol, trimethylol propane and pentaerythritol with saturated acids, and these esters are commonly used in applications such as refrigeration oils, compressor fluids and aviation turbine lubricants. They can be described as primary polyol esters since the esterification occurs on a primary hydroxyl of the polyol (Figure 1). Many saturated NPEs have excellent thermo-oxidative stability, good low temperature properties and are slower to hydrolyze than natural esters. Nonetheless, this hydrolysis is a limitation on their use in applications where there is a risk of water ingress into the lubricant.

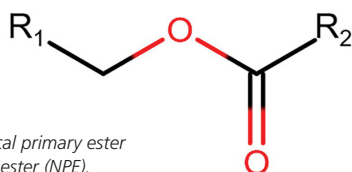


Figure 1: Classical primary ester of a neo-polyol ester (NPE).

There is a vast array of polyols available beyond those used for the manufacture of NPEs. By carefully selecting the choice of polyol, it is possible to design a wide range of secondary polyol esters. A simplistic structure for an SPE™ bond is shown (Figure 2).

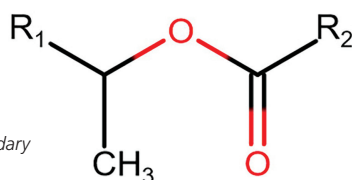


Figure 2: Secondary ester of an SPE.

The choice of polyol and acid, and indeed their mixtures, can lead to a very wide range of SPE products which have low viscosities or very high viscosities, and these can be saturated or unsaturated SPEs. Their functional and tribological characteristics can be controlled to a degree, by manipulating the polymer architecture. It is therefore possible to tailor this chemistry to design base oils for a specific application. This paper reports on SPEs exhibiting viscosities in the range ISO VG 32 to 100.

Properties and Functional Aspects

The lightly branched SPE structures offer a significant increase in the hydrolytic stability of the ester

bond and improves low temperature properties. Because of this structural feature, SPE base oils can utilise saturated fatty acids in their design without sacrificing cold temperature performance in contrast to, for example, natural esters in which a high saturated fatty acid content results in high pour points or solidification at room temperature. Furthermore, for the saturated SPEs this leads to more thermo-oxidatively stable products due to the absence of olefinic moieties in their structures. Although unsaturated esters are known to be more prone to oxidation, the oxygen-rich structure of unsaturated SPEs results in minimal or no deposit formation when they thermally degrade. This is also a well-known feature of PAGs. The high polarity of SPEs and PAGs facilitates the solubilisation of dangerous oxidation by-products that can deposit on equipment surfaces. This functionality is an important benefit over conventional mineral oils which can degrade to form insoluble polar deposits in the non-polar parent base oil that may lead to varnish formation on surfaces and result in equipment failure. This issue can be mitigated by including SPEs as additives or co-base oils in formulations where the primary base oil is a hydrocarbon.

The viscosity indices of SPEs are also high, in part due to the choice of polyol in the backbone such that their viscosity indices are similar to the high values associated with PAGs. Typical physical properties for structures in the ISO VG 32-100 range are shown in Table 2.

	32S	46S	46U	68S	68U	100S
Kin. Viscosity at 40°C, mm ² /sec	29.5	44.2	53.6	69.4	67.0	96.9
Kin. Viscosity at 100°C, mm ² /sec	6.1	8.6	10.7	12.1	13.0	15.5
Viscosity Index	162	177	196	173	198	170
Pour Point, °C	-51	-42	-24	-33	-39	-36
Density, g/cm ³	0.97	0.96	0.97	0.95	0.95	0.93
Flash Point (COC), °C	236	235	300	248	296	262
Biodegradation, %, OECD 301B	>80	>80	>80	>80	>80	>80
Biobased content, %	63	50	76	59	65	65

Table 2: SPEs derived from saturated (S) and unsaturated (U) acids.

These hybrid structures also possess excellent biodegradation profiles with values measured up to 95% over a 28-day period using OECD 301B test method. Their bio-based content is high (Table 2), and they are non-bioaccumulating (OECD 117) and non-toxic (OECD 201, OECD 202, OECD 203, OECD 236). Therefore, their environmental and physical properties make them an excellent choice for formulating modern bio-lubricants. Moreover, SPE base oils are accredited (NSF HX-1) for use as components in finished food grade lubricants (H1) intended for use in food processing plants where there is the potential of incidental food contact. In addition, some grades are on the EU Ecolabel LuSC-list and addition of the others are anticipated in Q1 2023. Inclusion on the LuSC-list means the oils have passed third party testing to meet strict biocontent, biodegradation, bioaccumulation, and sustainability requirements. Lubricant formulators can select LuSC-list approved components for use in their finished lubricant products in order for them to be considered Environmentally Acceptable Lubricants (EALs) and meet Vessel Incidental Discharge Act (VIDA) requirements.

Compatibility and Solubility

In solubility studies, SPE base oils show excellent miscibility with API Group II-IV hydrocarbon base oils and common API Group V base oils such as synthetic esters and PAGs at ratios of 50:50 (v:v). Unlike conventional PAGs (derived from ethylene oxide and 1,2-propylene oxide), the excellent miscibility of SPEs in hydrocarbon base oils provides formulators with greater versatility in developing new formulated solutions.

An important characteristic of SPE base oils resulting from their polymer structure is the high level of material compatibility with the seals/gaskets and coatings/paints in equipment. Historically, operators were resistant to making the switch from petroleum-based oils to bio-based synthetic esters because of their poor compatibility with seals and gaskets

in equipment not designed for ester-based oils. Preliminary elastomer studies of SPE base oils on common elastomers such as acrylonitrile butadiene rubber (more commonly known as NBR) and fluorine kautschuk material (FKM) show good compatibility (Figures 3 and 4). Their compatibility with NBR elastomer shows mild swelling, and on FKM (Viton) they remain generally neutral over the one-week test duration.

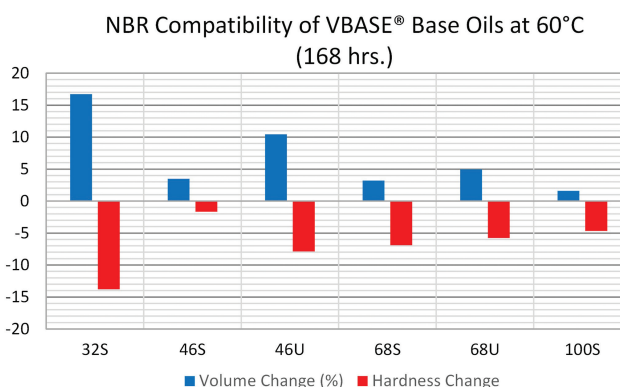


Figure 3: NBR Elastomer compatibility at 60°C for 168 hours.

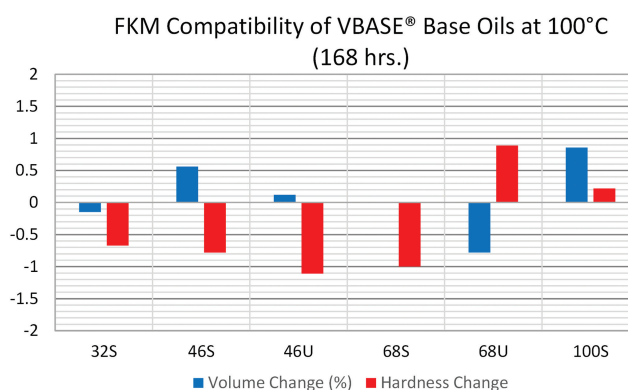


Figure 4: FKM Elastomer compatibility at 100°C for 168 hours.

Paint compatibility with SPE base oils was verified using Caterpillar Fluid Immersion Resistance Testing: Caterpillar 1E1952 [500 hours at 25±2°C] and John Deere Fluid Resistance Testing: John Deere JDM F17 [24 hours at 23±3°C]. Testing under both protocols saw no blistering, discolouration, delamination, or corrosion.

Fire Resistance

SPE base oils are an alternative to unsaturated esters and PAGs in formulating anhydrous fire-resistant hydraulic fluids (HFD-U fluids) which are commonly used in the steel and aluminium processing industries. Unsaturated esters such as trimethylolpropane trioleate offer high fire points but are prone to oxidation in high temperature equipment. PAGs are oxidatively and hydrolytically more stable but require careful conversion practices when transitioning equipment from a petroleum oil to a PAG. The hybrid functionality of SPEs can provide the high performance of PAGs while being compatible with petroleum oils. Table 3 shows fire resistance performance data of two SPE base oils (ISO-46 saturated and 68 unsaturated).

	Test Method	46S Base oil	68U Base oil	MIL-PRF-5606 Hydraulic Fluid Specification	MIL-PRF-83282 FR Hydraulic Fluid Spec
Flash point, COC (°C)	ASTM D92	235	296	>102	>210
Fire point, (°C)	ASTM D92	264	322	>110	>235
Auto-ignition temp. (°C)	ASTM E659	391	408	>232	>354
Flame propagation rate (cm/sec)	ASTM D5306	0.09	0.09	<0.73	<0.21
Wick Flammability (cycles)	FTM-352	19	40	-	>10
High temp. high pressure spray ignition	FTM-6052	Non-flammable No ignition	Non-flammable No ignition	No specification	Fluid shall not continue to burn when source of ignition removed

Table 3: Fire resistance performance of ISO-46 and 68 SPE Base Oils.

Base oil 68U exhibits a high fire point, high flash point and autoignition temperature. Both grades performed well on tests for spray flammability per the US Federal Standard 791D (6052) High Temperature-High Pressure Spray Ignition test. In this test the oil is heated to 100°F (37.8°C) and pressurised to 1000 psig. The pressurised oil is sprayed through a nozzle as an oxyacetylene flame is applied. No ignition was observed, and the fluids were rated as non-flammable. In tests for flame propagation rate and wick lighting, both base oils exceeded the requirements specified for standard hydraulic fluids (MIL-PRF-5606) and for fire resistant (FR) aviation

hydraulic fluids (MIL-PRF-83282). SPE base oils are recommended for formulating industrial fire-resistant hydraulic fluids to meet Factory Mutual and ISO-12922 standards for fire resistant fluids.

Formulated Lubricants using SPEs

The excellent laboratory performance of SPE base oils led to a program to evaluate them in formulated lubricants and in equipment trials. As an example, a formulated hydro-turbine oil was developed, and its properties illustrated in Table 4. In oxidation stability tests (RPVOT and dry-TOST), the fluid exhibited excellent performance. Demulsibility and foaming characteristics were good, and the product demonstrated compatibility in ferrous and copper corrosion testing. This data coupled with their excellent environmental performance provided confidence in moving the technology from the laboratory into equipment trials.

	Method	Result
Kin. Visc. at 40°C, mm ² /sec	ASTM D445	58
Viscosity index	ASTM D2270	182
Flash point, °C	ASTM D93	254
Pour point, °C	ASTM D97	-18
RPVOT, min.	ASTM D2270	1240
Dry TOST, hours	ASTM D943	8000
Rust prevention	ASTM D665A/B	pass/pass
Copper corrosion	ASTM D130	1a
Demulsibility, ml	ASTM D1401	40-40-0
Foaming, ml, 5 mins	ASTM D892	0-0-0
Air release, mins	ASTM D3427	6.2
FZG failure stage	ASTM D5182	12+
Biodegradation, 10 days, %	OECD 301B	66
Biodegradation, 28 days, %	OECD 301B	81
Biobased Carbon (¹⁴ C %)	ASTM D6866	57

Table 4: Formulated Hydro-turbine oil using SPE Technology.

The Global Center of Excellence for GE Hydro Solutions in Birr, Switzerland verified the performance of the formulated turbine oil on a combined thrust guide bearing test rig (Figure 5).

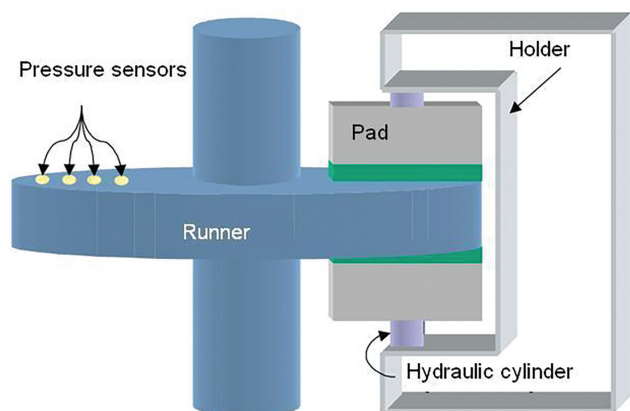


Figure 5: Schematic of test rig
(Image credit: GE Hydro Renewable Energy, GE Hydro Solutions).

The fluid performed well in all operating conditions including high load and low speed operation (mixed friction regime). There was no damage to bearing pad surface even after a high load (13Mpa) crash test. The rig could not induce failure of the fluid film. At speeds of 400-800 rpm and applied loads up to 13 Mpa, the fluid maintained a uniform hydrodynamic film, protecting the bearing and runner surfaces from damage. The next stage of the fluid assessment under real service conditions will be a trial at the Porjus Hydroelectric Power Station in Sweden. The Porjus Hydroelectric Power Station is Europe's pre-eminent hydropower research and development facility operated by Porjus Hydropower Centre Foundation, a joint collaboration between Andritz, GE Renewable Energy, and Vattenfall.

Conclusions

Esters remain an important class of base oil in formulating modern bio-lubricants; however, when designing for sustainability from the outset, there continues to be significant innovation in molecular and polymer design of base oils which are driving performance improvements while fulfilling the requirements for stricter environmental regulations aimed at creating safer and more sustainable lubricants. The novel secondary polyol ester (SPE) base oils are a new class of hybrid base oil that tailor

the combined functional advantages of PAGs and the environmental attributes of esters. Using the secondary ester bonds to slow hydrolysis and careful control of the molecular weight of hybrid components in the oil, high biodegradability, non-toxicity and non-bioaccumulation can be achieved while improving performance. Preliminary field performance testing of formulated lubricants using SPEs in equipment for hydropower turbines is demonstrating their potential as superior alternatives to conventional products. By choosing SPE base oils in their lubricants, formulators can now reduce their carbon footprint and meet sustainability goals while improving performance without compromise.



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This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Office of Energy Efficiency & Renewable Energy, Water Power Technologies Office under Award Number DE-SC0018751

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