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Breaking the Viscosity Ceiling: Development of Readily Biodegradable High Viscosity EAL Base Fluids

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Patech Europe

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- Background
- Modelling Techniques used to develop High viscosity Novel EAL Base Fluids
- Modeling Results VS Performance Data
- Compatibility with other base stocks.
- Conclusion

Sustainability for lubricants should consider an approach that sources raw materials that are easily replenished, reduces fluid waste, improves energy efficiency and lowers water usage **without compromising performance.**

ILMA Sustainability Definition.

The Objective is to use various Modelling Techniques to design a series high viscosity Eco-friendly Lubricant Base stocks that are:

- Develop Performance Lubricant Basestocks: Readily Biodegradable, Extremely good hydraulic and oxidative resistant, good lubricity performance, seal compatibility, etc.
- Models are then tested using conventional and modified ASTM test methods to demonstrated Modeling predictability.
- Since some of the high viscosity basestocks are used as viscosity modifiers, these Estes must be compatible in other biodegradable base stocks.

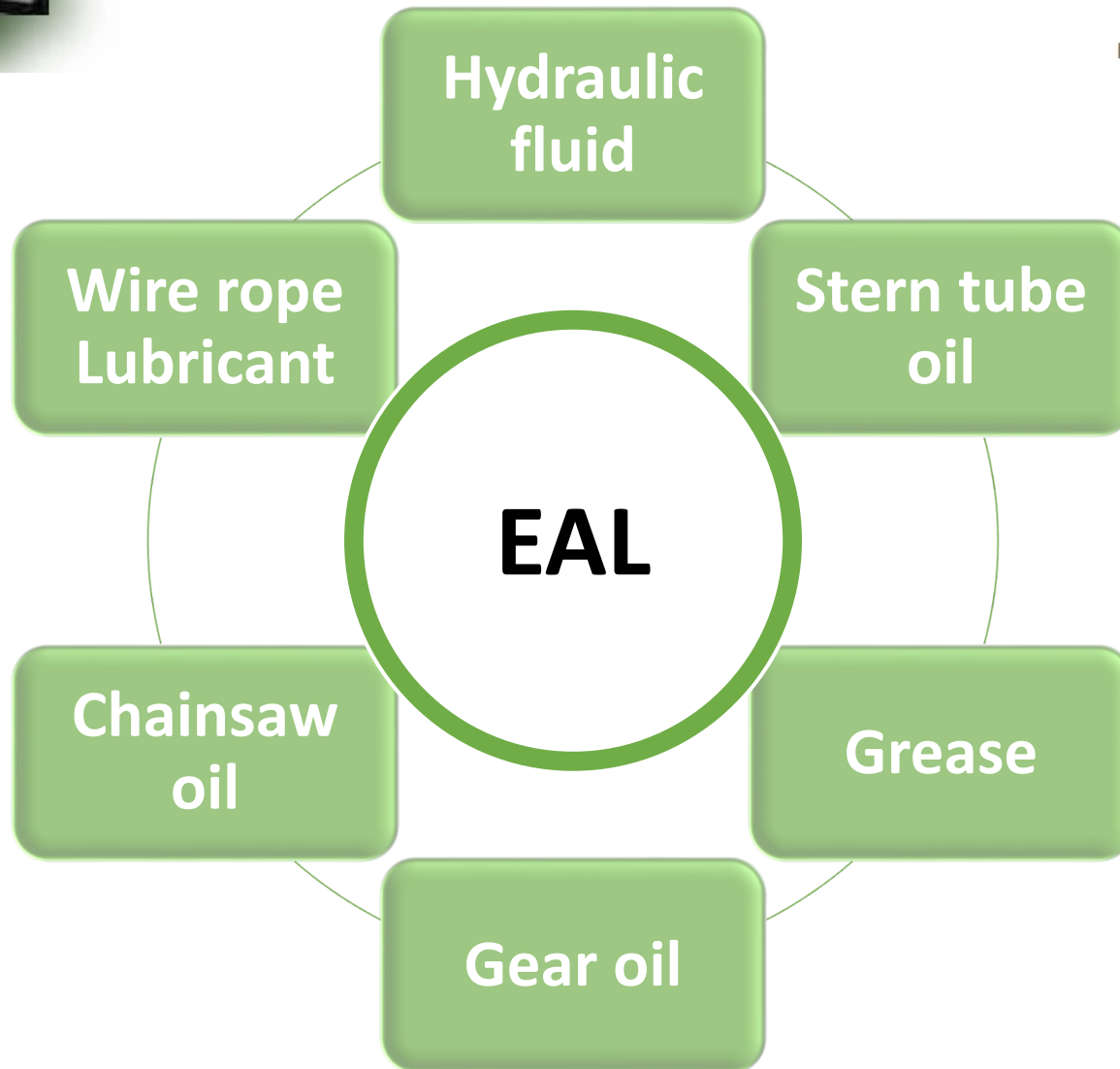
Background on EAL:

- EALs are environmentally acceptable lubricants that are **biodegradable**, **minimally toxic** and **not bioaccumulative** – as defined in Appendix A of the 2013 VGP to the environment.
- There is a clear trend towards a more responsible use of lubricants, and several legislations already limit the use of certain oils in some applications. (VGP in marine application)

EAL Applications

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- US EPA Vessel General Permit(VGP) is effective since 19th December 2013.
- ✓ The vessels $\geq 79\text{ft}$ in length enter US waters must be compliant with VGP.
- ✓ All lubricants using in all **oil to sea interfaces** must be EALs, unless technically infeasible.



Modelling Biodegradable Lubricant Basestocks

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What is modeling?: Models are methods of theoretical and computational analysis to mimic or predict the behavior of molecules. Modeling can expedite the development process. Building a database of performance test data is still required to make sure the level of predictability is high.

How do we model for lubricants?: Lubricants have very dynamic requirement. Therefore, we do need several modeling techniques that can predict the overall behavior these molecules when subjected to extreme environmental and physical stressors like:

- Temperature (extreme hot and cold)
- Oxidation Stability
- Pressure (lubricity and shear stability)
- Presence of moisture (hydrolytic stability)
- Microbiological Attack (biodegradability)

Basic Properties

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Palub	Saturation	KVis 40°C	KVis 100°C	Viscosity Index	Pour Point	Flash Point
EF-1000S	Saturated	1000	90	172	-21	295
EF-1000U	Unsaturated	1000	108	205	-24	320
EF-3000S	Saturated	3000	230	205	-9	304

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Modeling For Biodegradability

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Biodegradation is chemical breakdown or transformation of a substance caused by micro-organisms (bacteria, fungi) or their enzymes.

There are two extents of biodegradation of a substance:

Primary biodegradation

- Modification of some physical and chemical properties of the substance caused by activity of micro-organisms.

Ultimate biodegradation

- Total utilization of the substance resulted in its conversion into carbon dioxide (CO_2) or methane (CH_4), water (H_2O), mineral salts and microbial cellular constituents (biomass).



Biodegradability and Bio-accumulation Limits

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Biodegradability(OECD 301 A-F)

Readily biodegradable

≥ 60%

Inherently biodegradable

< 60% and ≥ 20%

Non-biodegradable

< 20%

Cumulative mass percentage(%w/w) limit for substances in the product	ALL	PLL	TLL	Grease ALL,PLL,TLL
Readily biodegradable	> 90	> 75	> 95	> 80
Inherently biodegradable	≤ 10	≤ 25	≤ 5	≤ 20
Non-biodegradable and non-bioaccumulative	≤ 5	≤ 20	≤ 5	≤ 15
Non-biodegradable and bioaccumulative	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1



Readily biodegradable: formulate without limitation



Inherently biodegradable: limited

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Biodegradability of Lubricant Esters

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Biochemistry steps of microbial attack on esters:

- Ester Hydrolysis
- β -oxidation of long chain hydrocarbons
- Oxygenase attack on aromatic nuclei

Main features that slow or reduce microbial breakdown are:

- Position and degree of branching
- Degree of saturation in the molecule
- Presence of aromatic groups
- High molecular weight

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The Structure Effect of Biodegradation

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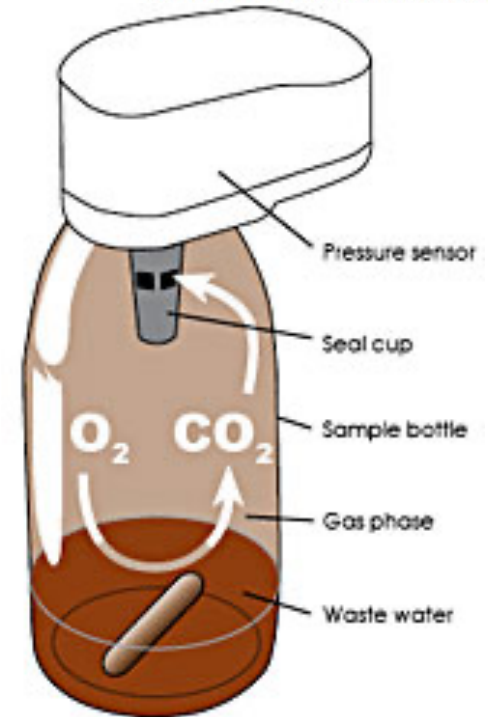
	Value	Biodegradability
Molecular Weight	↗	↘
Branch	↗	↘
Ester group	↗	↗
Ether	↗	↘
Hydroxyl group	↗	↗
Carboxyl acid Group	↗	↗

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OECD 301F Test

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- Biodegradation % = $\frac{\text{BOD}_{\text{test item}} - \text{BOD}_{\text{blank}}}{\text{ThOD}} \times 100\%$
- ThOD : Theoretical oxygen demand

LuSC list

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➤ LuSC list

Palub	Biodegradability%	LuSC-list
EF-1000S	>60%	Dosage without limitation
EF-1000U	>60%	Dosage without limitation
EF-3000S	>60%	Dosage without limitation

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Modeling for Hydrolytic Stability

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Limitation of current base fluids

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	Biodegradable	Potential for bioaccumulation	Toxicity	Viscosity index	Pour point	Lubricity	Thermal oxidative stability	Hydrolytic stability
Mineral oil	No	Yes	Yes	Poor	High	Poor	Poor	Good
PAO	Limited	No	No	Medium	Low	Medium	Good	Good
PAG	Yes	Low	Low	Good	Medium	Good	Medium	Good
Ester	Yes	No	No	Good	Low	Good	Good	Poor

In comparison with other basestocks, Esters have most acceptable performance criteria except for Hydrolytic stability.



Model of Ester Hydrolysis - Taft Equation

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Taft equation :
$$\log \frac{k_s}{k_0} = \rho^* \sigma^* + \delta E_s$$

E_s : Steric substituent constant

σ^* : Polar substituent constant

δ : Steric sensitivity factor

ρ^* : Polar sensitivity factor

k_s : Rate constant for ester with substituent

k_0 : Rate constant for ester of methanol and Formic acid

- Substituent position effect
- Chain length effect
- Branch Effect
- pH Effect



Beverage Bottle Hydrolytic Test

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Method: ASTM D2619-09(modified *)

Reaction temp.: $93 \pm 0.5^{\circ}\text{C}$

Testing time:

48 hours(Regular)

400 hours(Modified)

Sample weight: 75g

Water weight: 25g

Metal: Copper strip



* The regular testing time is 48 hours. We extends testing from 48 hours to 400 hours to simulate the severe condition.

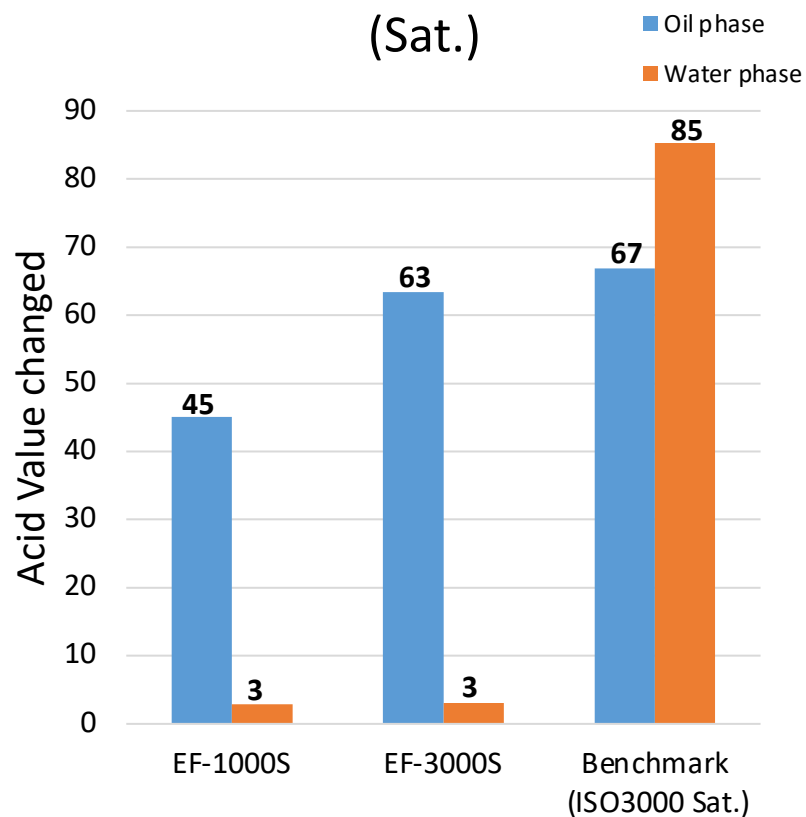
Hydrolytic Stability Test

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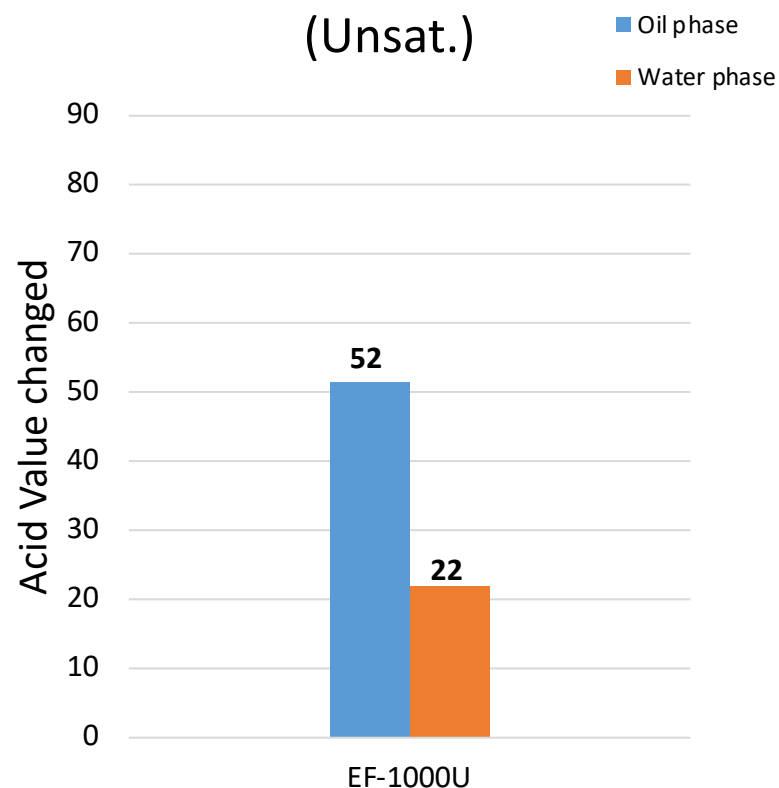
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➤ **Hydrolysis test** : extend the testing time to 400 hours

ASTM D2619
(Sat.)



ASTM D2619
(Unsat.)





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Modeling for Oxidation Stability

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Reactive Hydrogen Calculation

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- Thermal oxidation stability could be predicted by a simple reactive hydrogen calculation.

Reactive hydrogen:
the hydrogen atom on the secondary and tertiary carbons.



Reactive Hydrogen content(mole/100g) =

$$\frac{\text{Total Reactive Hydrogen Number} \times 100}{\text{molecular weight}}$$

Activation Energy Calculation – Kinetic Parameter

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Several literatures demonstrate the kinetic parameter of reaction could be estimated by thermal analysis e.g., DTA, TGA, and DSC.

- **Activation energy** is a very important kinetic parameter to determine the reaction occurs easily or not.

$$t_f = \frac{1}{Z_{id}} e^{E_{id}/RT_{id}}$$

- In this study, we use high-pressure DSC(PDSC) to measure the oxidation onset temperature (OOT) under different heating rate and calculate the **activation energy** of lubricant.

Oxidative Stability

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The relationship between activation energy, oxidation time and reactive hydrogen in comparison to DSC OOT.

	Reactive Hydrogen (mole/100g)	$E_{id}(KJmol^{-1})$	tf, cal. at 190°C (min)	DSC test result at 190°C(min)
PMA-isoC13	7.61	83.41	2.40	1.21
PMA-isoC9	3.88	125.83	10.22	10.07
DPE-isoC9	4.21	106.44	4.31	5.97

Reactive Hydrogen ↓



Activation energy ↑
Time to oxidation ↑



Effects on Thermal and Oxidative Stability of Ester

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Effects on Thermal and Oxidative Stability

Effect	Thermal & Oxidative Stability
β hydrogen	Without β hydrogen, Stability $\uparrow$ Polyol ester > Diester
C-H type	Stability : $\text{CH}_3 > \text{CH}_2 > \text{CH}$ ● Branch > Linear (PDSC) ● PE > DiPE > TMP > NPG ● Short chain > long chain
Olefinic unsaturation	Unsaturation $\uparrow$ Stability $\downarrow$
Aromatic	With aromatic Stability $\uparrow$

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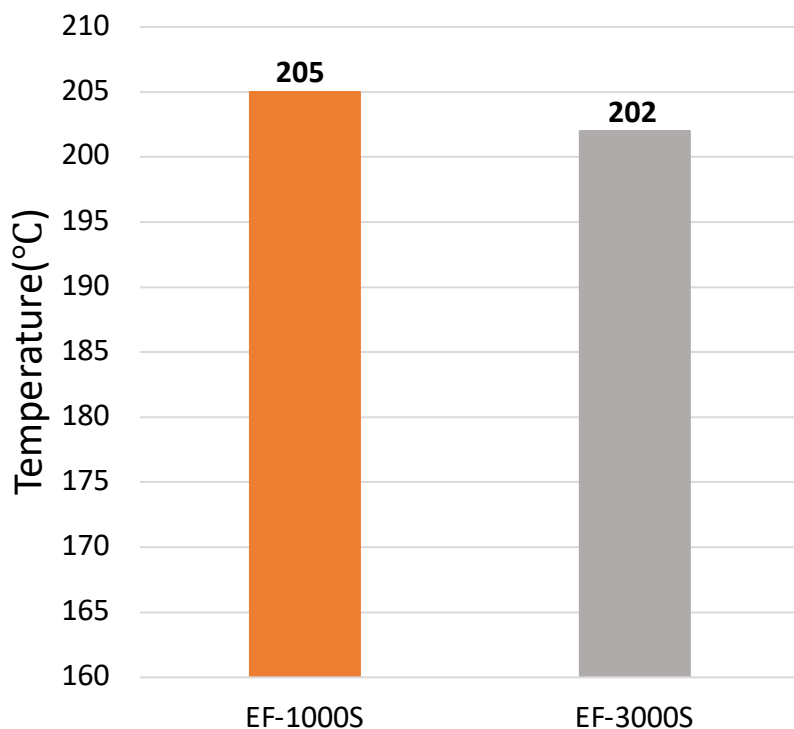
Oxidation Stability Test

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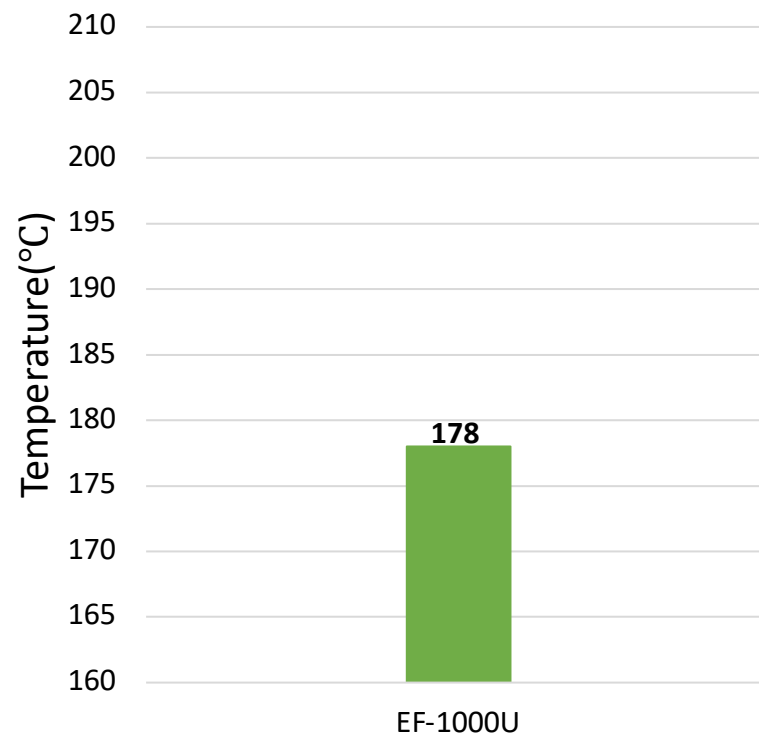
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➤ Oxidation Stability Test: ASTM E2009 Oxidative Onset Temperature (OOT)

ASTM E2009
(Sat.)



ASTM E2009
(Unsat.)





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Compatibility with other Base Stocks

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Compatibility Test with PAO2

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➤ Compatibility Palub with PAO2

	ISO grade	Compatibility @ RT	KVis 40°C	KVis 100°C	Viscosity Index	Pour Point
EF-1000S : PAO2	22	✓	20	5.0	190	<-60
	320	✓	313	38	170	-33
EF-1000U : PAO2	22	✓	20	5.2	206	<-60
	320	✓	310	44	202	-36
EF-3000S : PAO2	22	✓	23	6.1	235	<-60
	320	✓	322	45	198	-33
	1000	✓	900	95	197	-21

Compatibility Test with PAO4

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➤ Compatibility Palub with PAO4

	ISO grade	Compatibility @ RT	KVis 40°C	KVis 100°C	Viscosity Index	Pour Point
EF-1000S : PAO4	22	✓	23	5.1	149	<-60
	320	✓	330	38	164	-27
EF-1000U : PAO4	22	Incompatible	-	-	-	-
	68	✓	66	11	161	-42
	320	✓	300	49	184	-30
EF-3000S : PAO4	22	✓	21	4.7	143	<-60
	320	✓	310	40	184	-30
	1500	✓	1500	138	200	-15

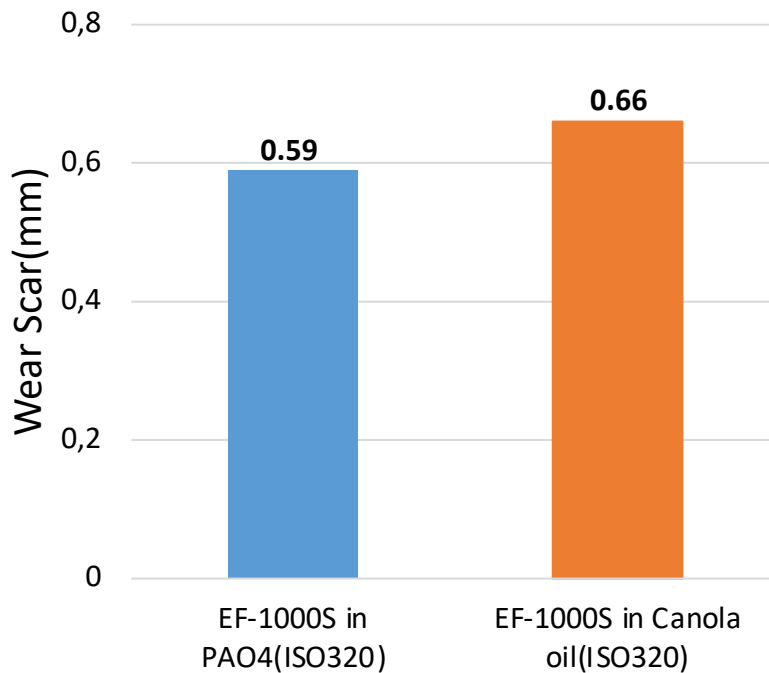
4-Ball Lubricity Test

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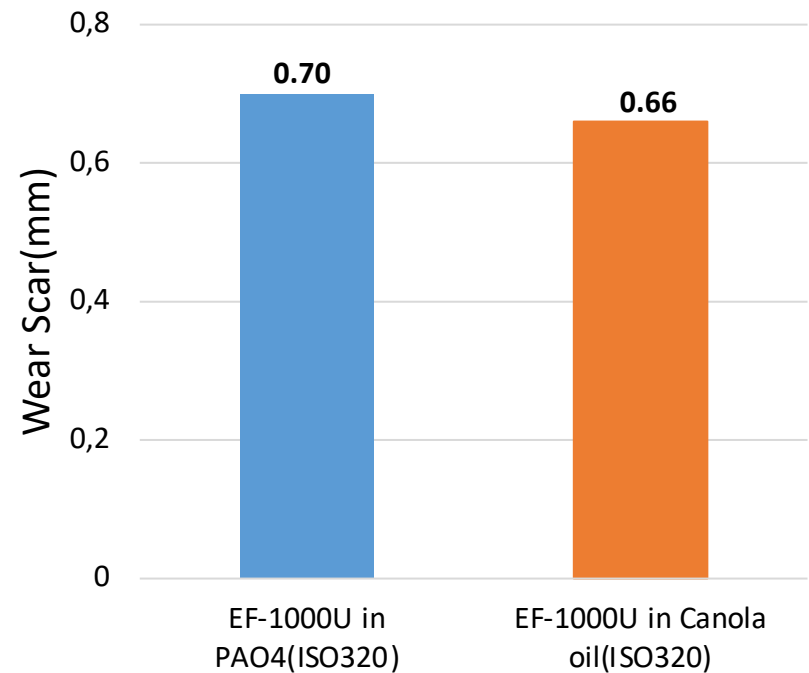
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➤ 4-Ball Anti-wear test : Palub EF-1000 in PAO4 / Vegetable oil (ISO320)

4-Ball Anti-wear Test
(Sat.)



4-Ball Anti-wear Test
(Unsat.)



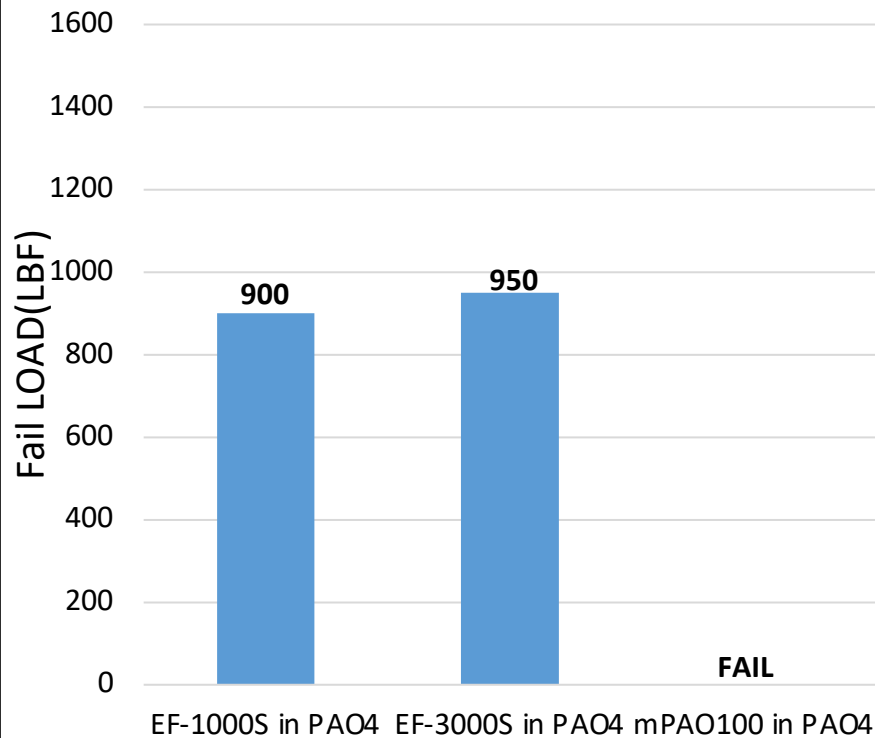
Falex P/V Lubricity Test

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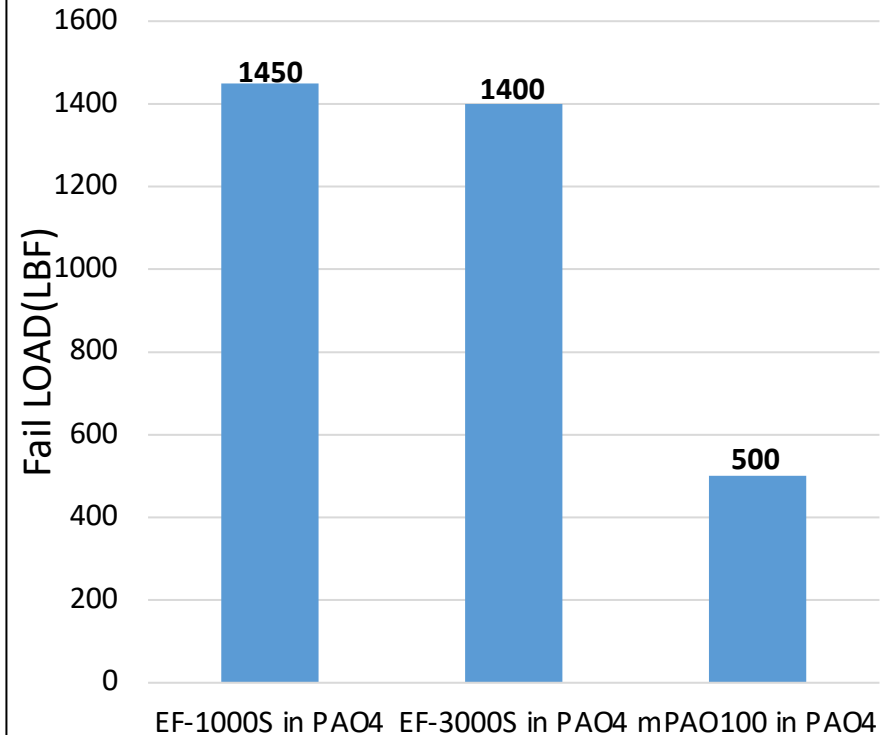
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➤ Falex EP test (Sat.):

Falex P/V Extreme Pressure Test
(ISO22)



Falex P/V Extreme Pressure Test
(ISO320)

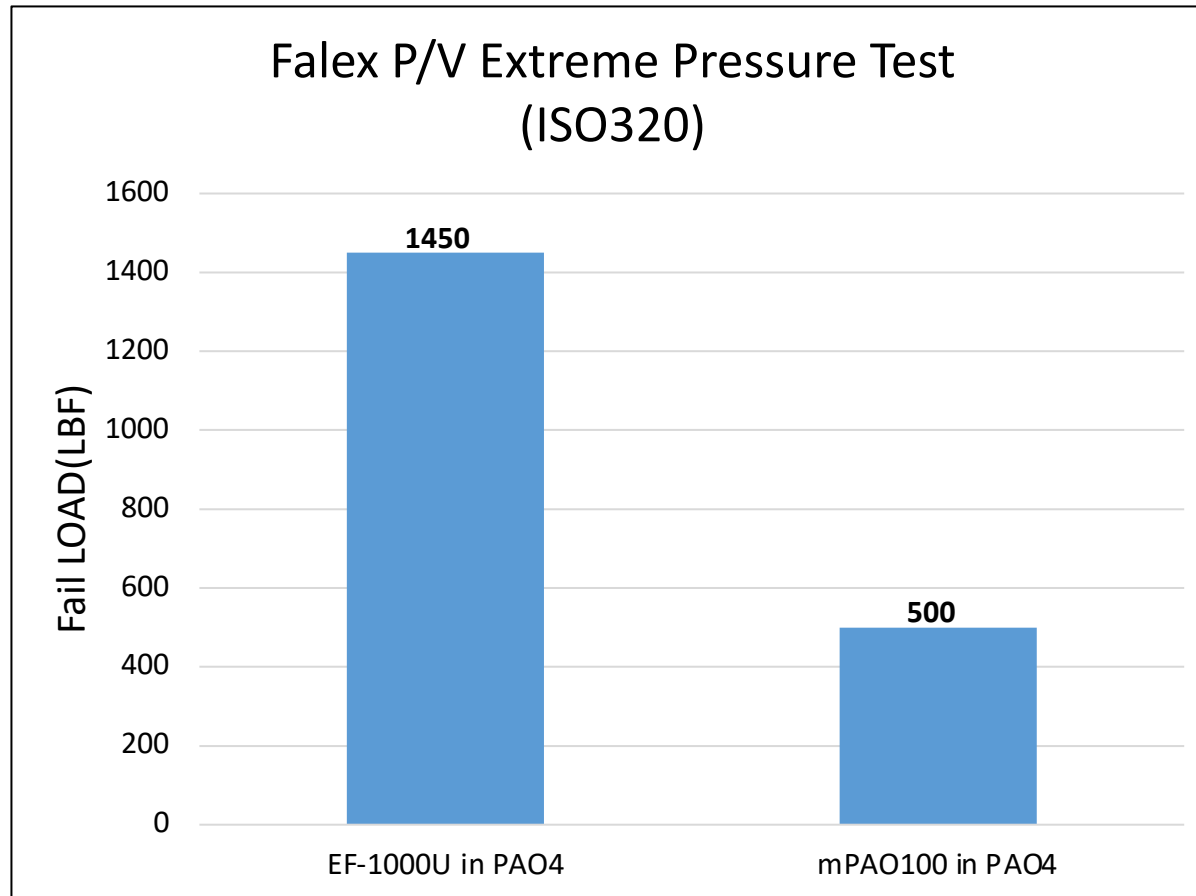


Falex P/V Lubricity Test

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➤ Falex EP test (Unsat.) :



Modeling Derived Readily Biodegradable Palub ISO1000 and ISO3000 synthetic esters have the following benefits:

Saturated esters

- Excellent Hydrolytic stability
- Excellent thermal oxidative stability
- Low aquatic toxicity
- Not bio-accumulating
- Biodegradable

Unsaturated esters

- High flash point
- Fire Resistant
- Good hydrolytic stability
- Low aquatic toxicity
- Not bio-accumulating
- Biodegradable



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Thanks For Your Attention!!

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