Advantages of synthetic ester base oils – reasons for growth

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STLE Annual Meeting – May 22, 2019

OXEA in brief

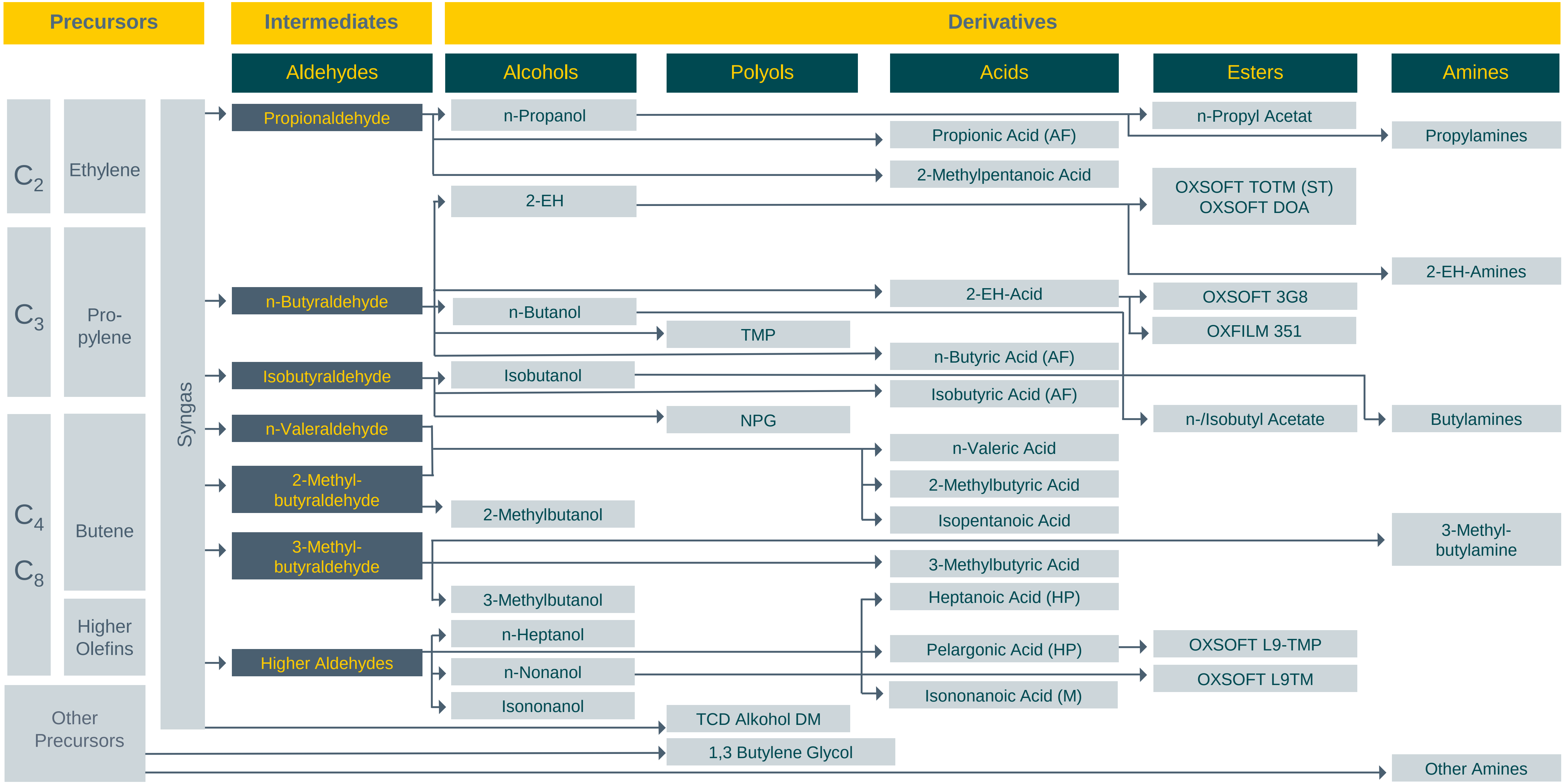
Launch:	March 1, 2007
Owner:	Oman Oil Company (OOC)
Employees:	approx 1,400
Sales:	approx € 1,2 billion
Products:	Oxo-Intermediates and Oxo-Derivatives, such as Aldehydes, Alcohols, Esters, Carboxylic Acids, Specialty Esters, Polyols, Amines

Global Presence

Production Sites

- Bishop *approx. 35*
- Bay City *approx. 180*
- Amsterdam *approx. 25*
- Oberhausen *approx. 900*
- Marl *approx. 70*
- Nanjing *approx. 50*

OXEA's integrated production platform



Esters and their properties

OXEA the oxo people

Natural oils	Synthetic esters	
	chemically modified natural oils *e.g. by (trans)esterification, hydrogenation epoxidation, dimerization, ozonolysis, hydroformylation, metathesis, …*	petrochemicals

low thermal stability

low oxidative stability

low hydrolytic stability

→

excellent thermal stability

excellent oxidative stability

very good hydrolytic stability

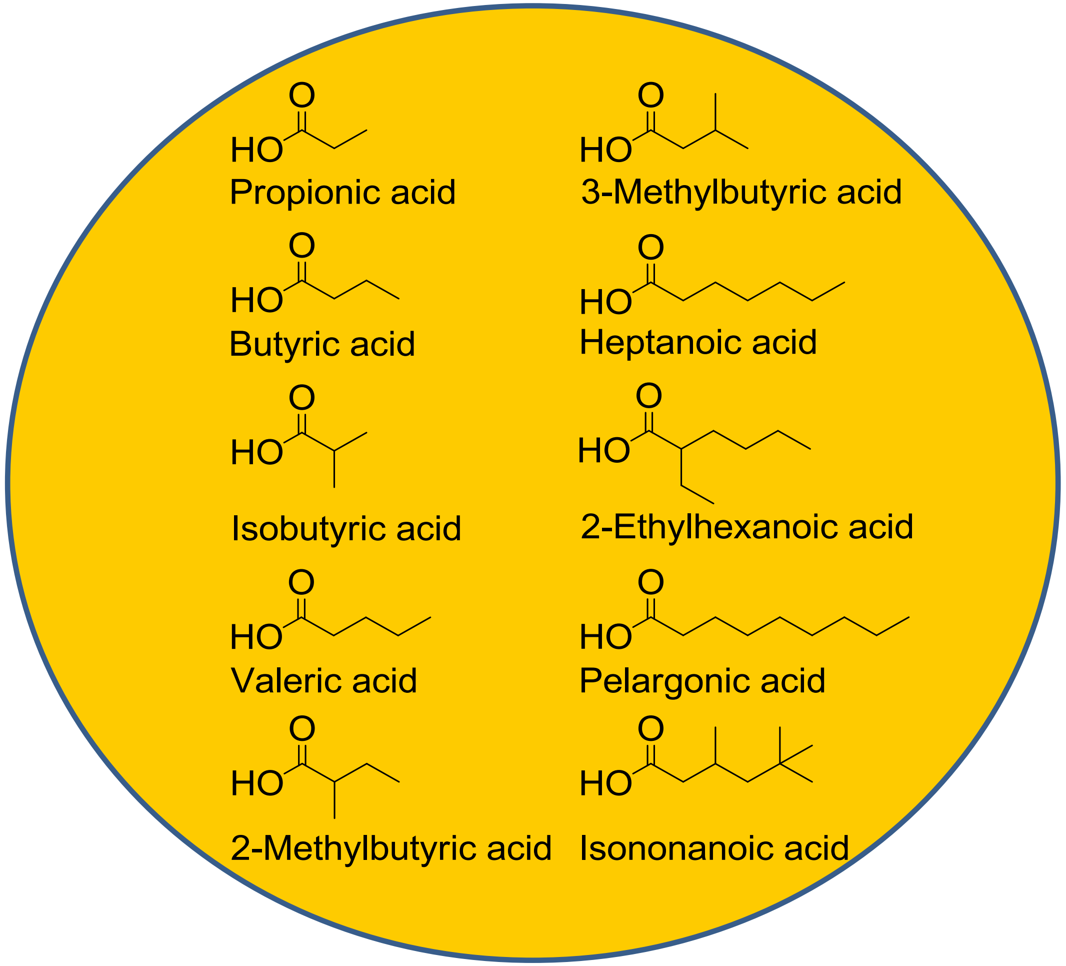
biobased	completely to partially biobased	non-biobased
(readily) biodegradable		

Base oil properties

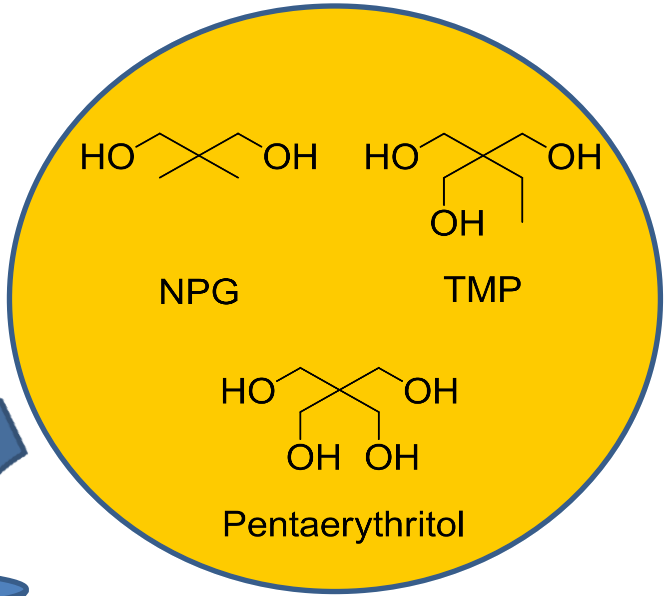
	Mineral oil	PAO	PAG	Monoester	Diester	Aromatic ester	Polyolester
viscosity-temperature	[illegible]	+	++	++	++	--	++
low temperature fluidity	--	+++	++	+++	+++	-	++
high temperature stability	--	[illegible]	+	[illegible]	+	+	++
low volatility/evaporation loss	--	[illegible]	+	-	+++	+++	+++
oxidation stability	-	++	+	+	+	-	++
frictional characteristics	-	+	[illegible]	+	+++	+	++
biodegradability	--	-	-	+++	+++	--	++
hydrolytic stability	+++	++	++	--	-	--	-
additive solubility	+++	[illegible]	--	[illegible]	++	++	++
elastomer compatibility	+++	+	++	--	--	--	-
paint/finish compatibility	[illegible]	+++	--	--	--	--	+
petroleum compatibility	+++	+++	--	+	[illegible]	+	+
initial cost	+++	++	+	+	+	+	+

still an oversimplification!

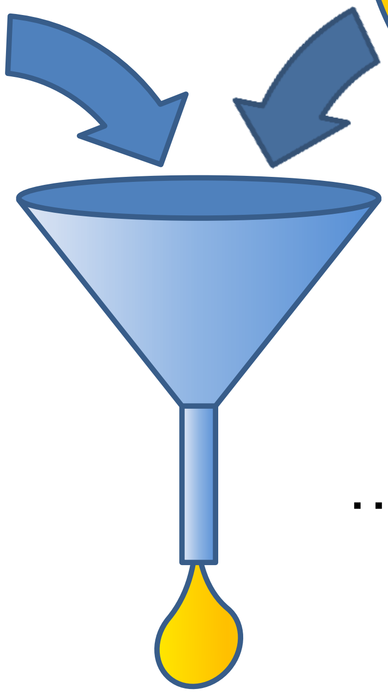
Due to the variety of possible combinations of polyols and carboxylic acids…



Synthetic Carboxylic Acids



Polyols



…polyolesters with tailor-made properties can be produced

Ester properties are depending on the acid used

	Viscosity [mm²/s]	
	40 °C	100 °C
NPG + nC5	3,6	1,4
NPG + nC7	5,6	1,9
NPG + 2-EH	7,5	2,1
NPG + nC9	8,7	2,6
TMP + nC7	13,8	3,4
TMP + 2-EH	25,2	4,3
TMP + nC9	20,0	4,5
PE + nC5	15,9	3,6
PE + 2-MB	25,7	4,4
PE + nC7	22,5	4,6
PE + 2-EH	45,7	6,3
PE + nC9	31,8	6,0
PE + iC9	116,0	11,5

Viscosity:

- increasing with chain length and branching
- NPG<TMP<PE

Ester properties are depending on the acid used

	Viscosity [mm²/s]		Viscosity
	40 °C	100 °C	index
NPG + nC5	3,6	1,4	-
NPG + nC7	5,6	1,9	-
NPG + 2-EH	7,5	2,1	65
NPG + nC9	8,7	2,6	139
TMP + nC7	13,8	3,4	122
TMP + 2-EH	25,2	4,3	55
TMP + nC9	20,0	4,5	142
PE + nC5	15,9	3,6	108
PE + 2-MB	25,7	4,4	63
PE + nC7	22,5	4,6	121
PE + 2-EH	45,7	6,3	79
PE + nC9	31,8	6,0	137
PE + iC9	116,0	11,5	83

Viscosity index:

- increasing with chain length
- higher with linear/lower with branched acids

Ester properties are depending on the acid used

	Viscosity [mm²/s]		Viscosity	Density
	40 °C	100 °C	index	[g/cm³]
NPG + nC5	3,6	1,4	-	0,9458
NPG + nC7	5,6	1,9	-	0,9259
NPG + 2-EH	7,5	2,1	65	0,9156
NPG + nC9	8,7	2,6	139	0,9131
TMP + nC7	13,8	3,4	122	0,9598
TMP + 2-EH	25,2	4,3	55	0,9469
TMP + nC9	20,0	4,5	142	0,9401
PE + nC5	15,9	3,6	108	1,019
PE + 2-MB	25,7	4,4	63	1,0151
PE + nC7	22,5	4,6	121	0,9798
PE + 2-EH	45,7	6,3	79	0,9636
PE + nC9	31,8	6,0	137	0,9544
PE + iC9	116,0	11,5	83	0,9523

Density:

- decreasing with chain length and branching

Ester properties are depending on the acid used

	Viscosity [mm²/s]		Viscosity	Density	Pour point
	40 °C	100 °C	index	[g/cm³]	[°C]
NPG + nC5	3,6	1,4	-	0,9458	-89
NPG + nC7	5,6	1,9	-	0,9259	-85
NPG + 2-EH	7,5	2,1	65	0,9156	-72
NPG + nC9	8,7	2,6	139	0,9131	-33
TMP + nC7	13,8	3,4	122	0,9598	-73
TMP + 2-EH	25,2	4,3	55	0,9469	-50
TMP + nC9	20,0	4,5	142	0,9401	-45
PE + nC5	15,9	3,6	108	1,019	-69
PE + 2-MB	25,7	4,4	63	1,0151	-33
PE + nC7	22,5	4,6	121	0,9798	-41
PE + 2-EH	45,7	6,3	79	0,9636	-11
PE + nC9	31,8	6,0	137	0,9544	1
PE + iC9	116,0	11,5	83	0,9523	-31

Pour point:

- usually increasing with chain length
- depending on the branching pattern

Ester properties are depending on the acid used

	Viscosity [mm²/s]		Viscosity	Density	Pour point	Flash point (COC)
	40 °C	100 °C	index	[g/cm³]	[°C]	[°C]
NPG + nC5	3,6	1,4	-	0,9458	-89	154 (CC)
NPG + nC7	5,6	1,9	-	0,9259	-85	190
NPG + 2-EH	7,5	2,1	65	0,9156	-72	180 (CC)
NPG + nC9	8,7	2,6	139	0,9131	-33	231
TMP + nC7	13,8	3,4	122	0,9598	-73	254
TMP + 2-EH	25,2	4,3	55	0,9469	-50	237
TMP + nC9	20,0	4,5	142	0,9401	-45	250
PE + nC5	15,9	3,6	108	1,019	-69	250
PE + 2-MB	25,7	4,4	63	1,0151	-33	230 (CC)
PE + nC7	22,5	4,6	121	0,9798	-41	263
PE + 2-EH	45,7	6,3	79	0,9636	-11	264
PE + nC9	31,8	6,0	137	0,9544	1	295
PE + iC9	116,0	11,5	83	0,9523	-31	271

Flash point:

- increasing with chain length
- NPG<TMP<PE

Ester properties are depending on the acid used

	Viscosity [mm²/s] 40 °C	Viscosity [mm²/s] 100 °C	Viscosity index	Density [g/cm³]	Pour point [°C]	Flash point (COC) [°C]	Readily biodegradable*
NPG + nC5	3,6	1,4	-	0,9458	-89	154 (CC)	
NPG + nC7	5,6	1,9	-	0,9259	-85	190	yes
NPG + 2-EH	7,5	2,1	65	0,9156	-72	180 (CC)	no
NPG + nC9	8,7	2,6	139	0,9131	-33	231	
TMP + nC7	13,8	3,4	122	0,9598	-73	254	yes
TMP + 2-EH	25,2	4,3	55	0,9469	-50	237	
TMP + nC9	20,0	4,5	142	0,9401	-45	250	yes
PE + nC5	15,9	3,6	108	1,019	-69	250	yes
PE + 2-MB	25,7	4,4	63	1,0151	-33	230 (CC)	
PE + nC7	22,5	4,6	121	0,9798	-41	263	yes
PE + 2-EH	45,7	6,3	79	0,9636	-11	264	no
PE + nC9	31,8	6,0	137	0,9544	1	295	yes
PE + iC9	116,0	11,5	83	0,9523	-31	271	no

*according to REACH registration

Biodegradability:

- decreasing with chain length and branching

Further properties

	Hydrolytic stability		Volatility	Oxidative stability		Thermal Stability Cincinnati Milacron			Wear 4-balls
	ASTM D2619		ASTM D5800 B	ASTM D2272	ASTM D943	ASTM D2070			ASTM D 4172/B
	TAN difference	Water acidity	NOACK	RPVOT	Dry TOST	Acidity change	Viscosity loss	Total sludge weight	scar diameter
	[mg KOH/g]	[mg KOH/g]	[%]	[min]	[h]	[mg KOH/g]	[%]	[mg/100 ml]	[mm]
NPG + nC7	0,03	0,18	-	77	177	1,03	4,7	12,2	0,57
TMP + nC9 (L9-TMP)	0,03	0,00	2,2	79	170	0,33	3,2	11,6	0,55
PE + nC9	0,14	1,13	0,5	77	179	0,24	2,4	2,8	0,56
Glycerin + nC9	0,54	1,29	4,4	68	201	0,64	5,1	22,8	0,57
TCD DM-nC9-Ester	0,28	1,46	3,9	30	52	0,19	4,3	5,0	0,48

Ester base fluids without any additives

very good hydrolytic stability

very low volatility

high oxidative & thermal stability

at very low viscosities

esp. for neopolyol esters (NPG, TMP, PE)

What is your definition of biolubricants?

Biolubricants

rather distinguish between

biobased	readily biodegradable
e.g. vegetable oils	*e.g. synthetic esters*
not necessarily readily biodegradable (e.g. BtL) or sustainable (e.g. food vs. fuel, palm oil)	not necessarily biobased
What is an acceptable biobased content?	*What is an acceptable degradation rate?*

non-toxic (hazardous compounds/SVHCs? aquatic toxicity?)

Definition of EALs according to VGP 2013

"Environmentally Acceptable Lubricants" means lubricants that are "biodegradable" and "minimally-toxic," and are "not bioaccumulative" as defined in this permit. For purposes of the VGP, products meeting the permit's definitions of being an "Environmentally Acceptable Lubricant" include those labeled by the following labeling programs: Blue Angel, European Ecolabel, Nordic Swan, the Swedish Standards SS 155434 and 155470, Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) requirements, and EPA's Design for the Environment (DfE).

-> biobased content not required by VGP

https://www3.epa.gov/npdes/pubs/vgp_permit2013.pdf

Definition of biodegradability according to EU Ecolabel 2019

the oxo people

'Readily biodegradable' means an arbitrary classification of chemicals which have passed certain specified screening tests for ultimate biodegradability; these tests are so stringent that it is assumed that such compounds will rapidly and completely biodegrade in aquatic environments under aerobic conditions. Substances are considered rapidly degradable in the environment if one of the following criteria holds true:

1. if, in 28-day ready biodegradation studies, at least the following levels of degradation are achieved:

- tests based on dissolved organic carbon: 70 %,
- tests based on oxygen depletion or carbon dioxide generation: 60 % of theoretical maximum.

These levels of biodegradation must be achieved within 10 days of the start of degradation which point is taken as the time when 10 % of the substance has been degraded, unless the substance is identified as an UVCB or as a complex, multi-constituent substance with structurally similar components. In this case, and where there is sufficient justification, the 10-day window condition may be waived and the pass level applied at 28 days; or

https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32018D1702&from=EN

Similar definition: https://www3.epa.gov/npdes/pubs/vgp_permit2013.pdf

Biodegradability

Biodegradability

readily biodegradable
(>60% in 28 days)

→ required for lubricants according to VGP and EU Ecolabel

inherently biodegradable
(>20 but <60% in 28 days)

non-biodegradable

Renewability requirements according to EU Ecolabel 2019

(a) In the specific case of renewable ingredients from palm oil or palm kernel oil, or derived from palm oil or palm kernel oil, 100 % w/w of the renewable ingredients used shall meet the requirements for sustainable production of a certification scheme that is a multi-stakeholder organisation with a broad membership, including NGOs, industry and government and that addresses environmental impacts on soil, biodiversity, organic carbon stocks and conservation of natural resources.

(b) If the term ‘bio-based’ or ‘bio-lubricant’ is used, the minimum bio-based carbon content in the final product shall be 25 % in accordance with EN 16807.

-> biobased content not required by EU Ecolabel 2019

-> sustainable production of palm oil derivatives needs to be certified

https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32018D1702&from=EN

Carboxylic acids based on Palm (Kernel) Oil

Natural fatty acid distribution in Palm Oil and Palm Kernel Oil (as triglycerides):

	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic
	C8	C10	C12	C14	C16	C18	C18:1	C18:2
Palm Oil				1.0%	43.5%	4.3%	36.6%	9.1%
Palm Kernel Oil	3.3%	3.4%	48.2%	16.2%	8.4%	2.5%	15.3%	2.3%
Coconut Oil	7%	8%	48%	16%	9.5%		6.5%	

EU Ecolabel requires certification of sustainable production of Palm (Kernel) Oil,

e.g. by RSPO

Currently, only 19% of global palm oil is certified by RSPO (https://www.rspo.org/)

Have you checked the origin of these acids used in your esters?

Petro- vs. biobased ester – an example

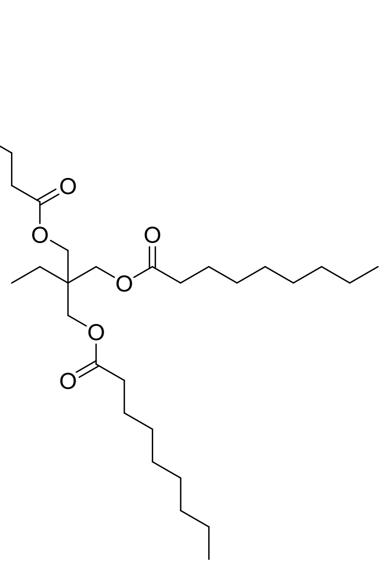
L9-TMP vs. C8/C10-TMP

both used in diverse lubricant applications:

engine oils (2 & 4 stroke), compressor oils, turbine oils,

hydraulic fluids, gear oils, chain oils, greases,

metalworking fluids, textile spinning fluids



C8/C10 acid

- derived from PKO or CNO → biobased
- sustainable?
- additional costs for certified sources
- supply can get tight (El Niño)
- volatile pricing

nC9 acid

- derived from α-olefin based on ethylene
- dedicated production using synthetic feedstocks
- reliable supply & pricing
- palm oil free

L9-TMP vs, C8/C10-TMP

Typical properties	Method	Units	L9-TMP* (CAS 126-57-8)	C8/C10-TMP* (CAS 91050-89-4)
Appearance	Visual	-	clear and bright	clear and bright
Water	ASTM E1064/E203	%	<0.03	0,02
Acid number	ASTM D974	mg KOH/g	<0.05	0,02
Colour	ASTM D5386	Hazen	<100	<100
Specific gravity @15.6°C	ASTM D4052	kg/l	0,94	0,94
Viscosity @40°C	ASTM D445	mm^2/s	20	19
Viscosity @100°C	ASTM D445	mm^2/s	4,5	4,3
Viscosity index	ASTM D2270	-	142	137
Thermal properties				
Noack volatility	CEC L-40-A	weight loss, wt%	**1,73**	2,42
Volatility @ 205°C (6.5 h)	ASTM D972	weight loss, wt%	**3,56**	4,29
Boiling point (50%)	ASTM D2887	°C	483	475
Flash point (COC)	ASTM D92	°C	250	257
Pour point	ASTM D5950	°C	-45	-48
Oxidative stability				
RPVOT	ASTM D2272	minutes	**79**	63
Dry TOST	ASTM D943	hours (to 2 mg KOH/g)	**201**	178
Biodegradability				
OECD 301B	28 days	%	**95**	80

*base fluid without any additives

comparable properties

both are readily biodegradable

both in compliance with EU Ecolabel

Take home message

- Properties of esters can be tuned by using different carboxylic acids
- Readily biodegradable esters are not necessarily biobased
- Biobased esters are not necessarily sustainable
- VGP & EU Ecolabel require readily biodegradable substances, no biobased content

Due to the versatility of esters, there is an appropriate solution for nearly any application

Any Questions?

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