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HIGH PERFORMANCE ANTIOXIDANTS FOR SYNTHETIC ESTERS

From jet engine oils
to high temperature industrial lubricants

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AGENDA

1. Neopolyol esters: thermo-oxidative stability
2. Dedicated antioxidant system
3. Application to jet engine oils
4. Extension to industrial lubricants
5. Conclusion

Neopolyol esters

Thermo-oxidative stability

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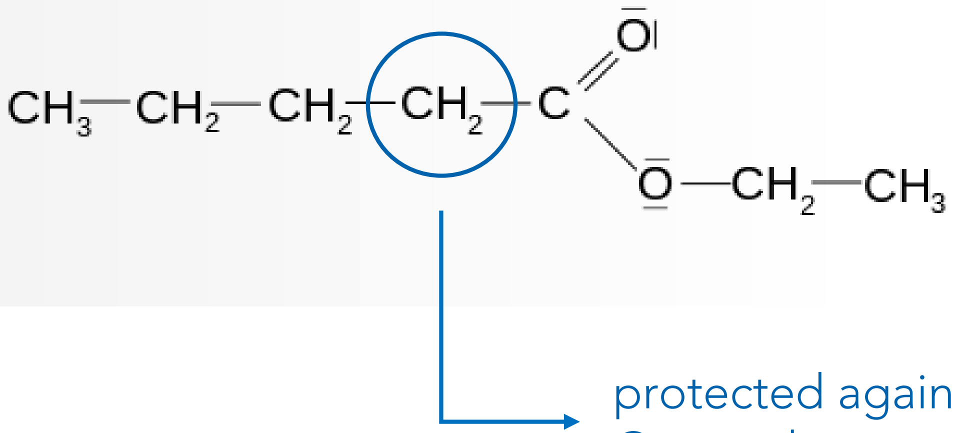
Synthetic esters

- High viscosity indices and good low temp properties, low volatility
- Anti-wear and friction modifying benefits
- Excellent thermo-oxidative stability
- Good solvency and detergency properties
- Compatibility with mineral base fluids
- Non dangerous, biodegradable, can be made of renewable carbon

Resistance to oxidation

Main oxidation initiation step: $RH + O_2 \longrightarrow R^\circ + HOO^\circ$

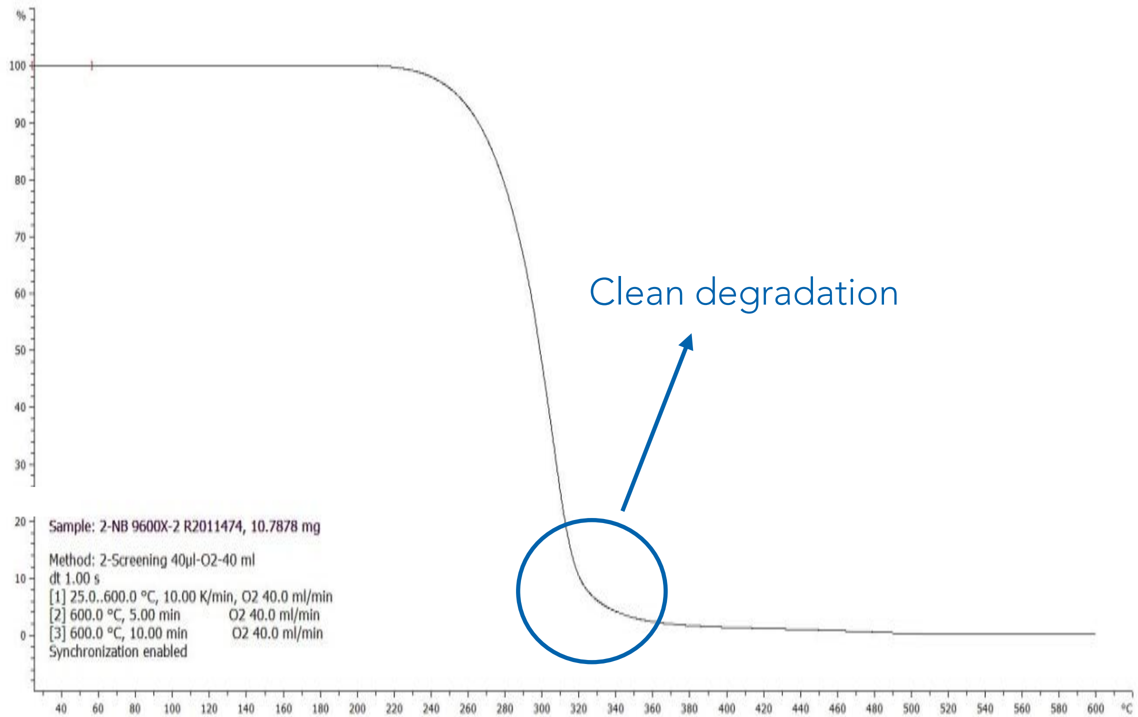
- Esters show less C-H sites than hydrocrabons
- Some C-H sites are stabilised by ester function



protected against O_2 attack

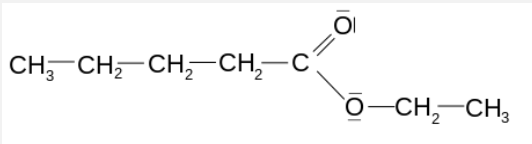
Cleanliness

- Esters tend to break down into light, volatile radicals
- Esters are mild detergents, they dissolve oxidation by-products

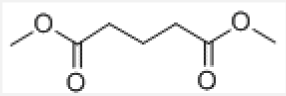


Neopolyol esters

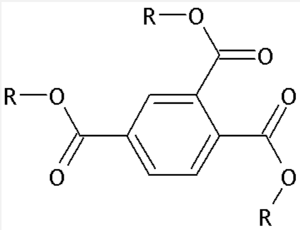
Monoesters

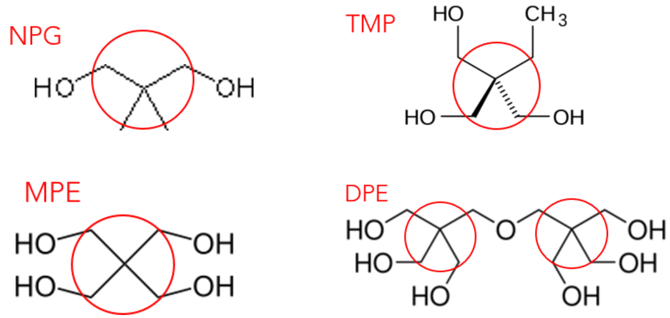


Diesters

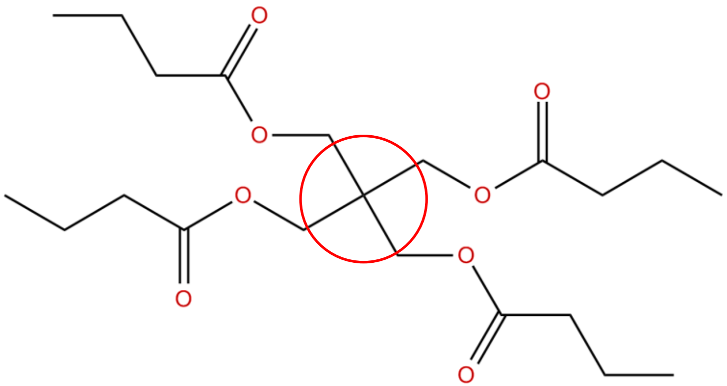


Trimellitate esters



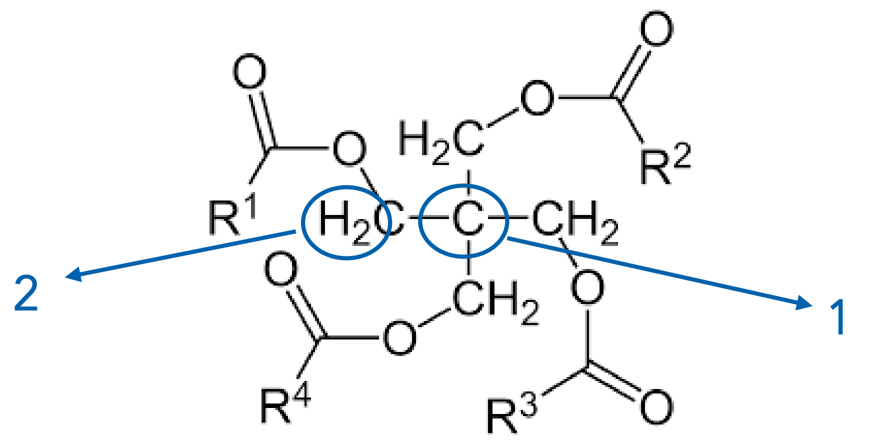


Neopentyl structure

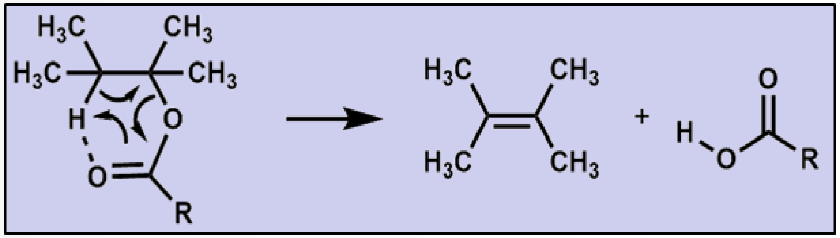


Neopolyol ester

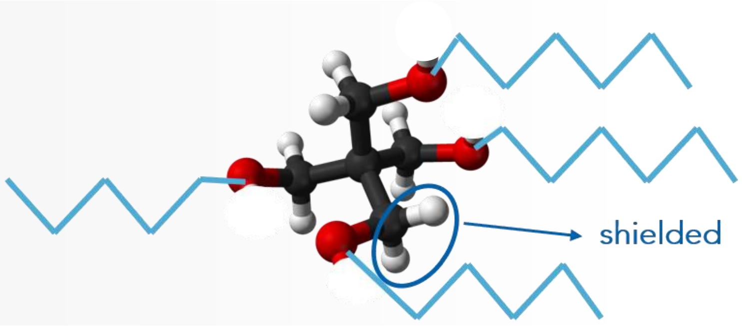
Neopolyol esters



1. No β-elimination is possible: thermal stability



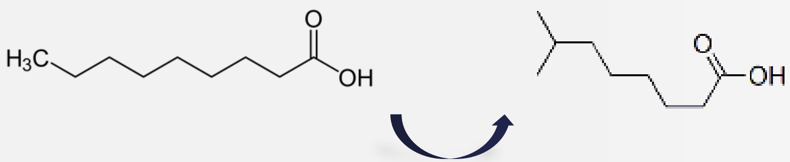
2. Alcohol $–CH_2$ are shielded by acid chains: oxidative stability



Acid chain branching

Primary	*Secondary*	*Tertiary*
98.0 kcal.	94.5 kcal	91.0 kcal
$R - CH_2 - H$	$R_2CH - H$	$R_3C - H$

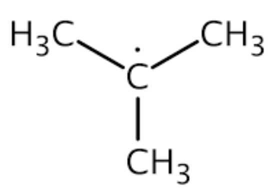
- H from $–CH_3$ are much more stable



3 H from $–CH_3$ out of 17

6 H from $–CH_3$ out of 17

- Branching increases the number of stable H sites, delivering improved resistance to oxidation



- Branching favors degradation into volatile fractions

Branched neopolyol esters

ASTM D4636 – 204C - Fully formulated fluids

Property	Unit	PAO 4	MOE	DIE	NPE	linear NPE	branched NPE
Viscosity at 40C	mm^2/s	17.3	3.2	11.6	13.8	29.6	94.1
Δ KV 40C	%	17.4	18.1	16.1	15	22	22.5
Δ Acid number	mg KOH/g	7.7	16	7.8	1.7	1.3	0.4
Δ Weight Steel Silver Aluminium Magnesium Copper	mg/cm^2	 0.28 0.24 0.33 -0.93 0.69	 0.45 0.18 0.16 -4.5 0.76	 0.06 0.03 0.01 0.01 0.17	 0.0 -0.05 -0.01 -0.01 0.14	 -0.03 -0.02 -0.01 -0.02 -0.02	 -0.05 -0.06 -0.08 -0.06 0.06
Deposit	mg/100 ml	438	1847	18	0.9	2.2	0.9



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Dedicated antioxidant system

The needs of the aviation industry

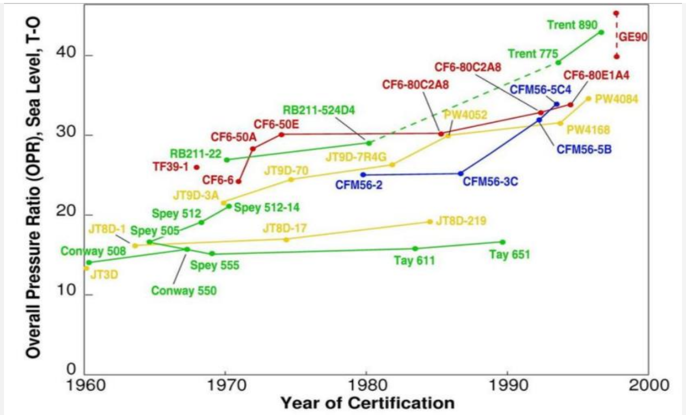

Figure 3.18: Gas turbine engine pressure ratio trends (Jane's Aeroengines, 1998)

- Operating temperatures of jet engines have been increasing
- Oils are exposed to higher temperatures and need to evacuate more heat

The need for improved stability has led to the development of a high molecular weight oligomer AO showing

- *reduced volatility*
- *improved thermal resistance*
- *improved stabilisation of free radicals*

Slower AO depletion
Increased activity

Goal is to achieve increased lubricant longevity, reduced evaporation, and improved resistance to deposit formation

Jet engine oils

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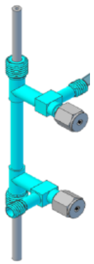
Test methods, performance

High Performance Capability vs **Standard Performance Capability**:

SAE AS 5780 HPC requires improved jet engine oil performance on resistance to thermo-oxidation, coking propensity, and in high temperature bearing test

ASTM D4636
Oxidation and corrosion
72h, 204C
Air flow : 5 l/h

	SPC	HPC
ΔKV %	15.7	12.3
ΔTAN mg KOH/g	1.10	1.15
Sediment mg/100 ml	1.2	0.07



SAE-ARP-5996
Hot Liquid Process Simulator
375C

	SPC	HPC
20 h (mg)	0.50	0.15
40 h (mg)	-	0.35

SPC products use classical AO
HPC products use oligomer AO

Test methods, performance

FED-STD-791 - 3411
Thermal stability
and corrosivity
96 h, 274C

FED-STD-791 – 3410
High T°C bearing test
Bulk: 199C
Bearing: max 260C
10,000 rpm

	SPC	HPC
ΔKV %	1.1	0.04
ΔTAN mg KOH/g	2.6	0.35
Metal mass mg/cm²	-0.2	0.02

	SPC	HPC
100 h Bearing demerit	45	-
200 h Bearing demerit	-	27

Test methods, performance

Vapour Phase Coking test 260C – 48 h		Engine test Aero-derivative turbine	
SPC	HPC	SPC	HPC
			

Oligomer AO technology must be used to comply with SAE-AS 5780 HPC

Extension to industrial applications

Extension to industrial applications

- Extreme industrial conditions: turbines, furnace conveyors, turbochargers, foundry equipment, etc.

- Conveyor chains (construction materials: glass fibers, cement, laminated particle board and flooring, plastics, ceramics, stretch film), etc.

→ Temperatures exceeding 300C

- Using NPE and oligomer AO technology improves performance in such applications too

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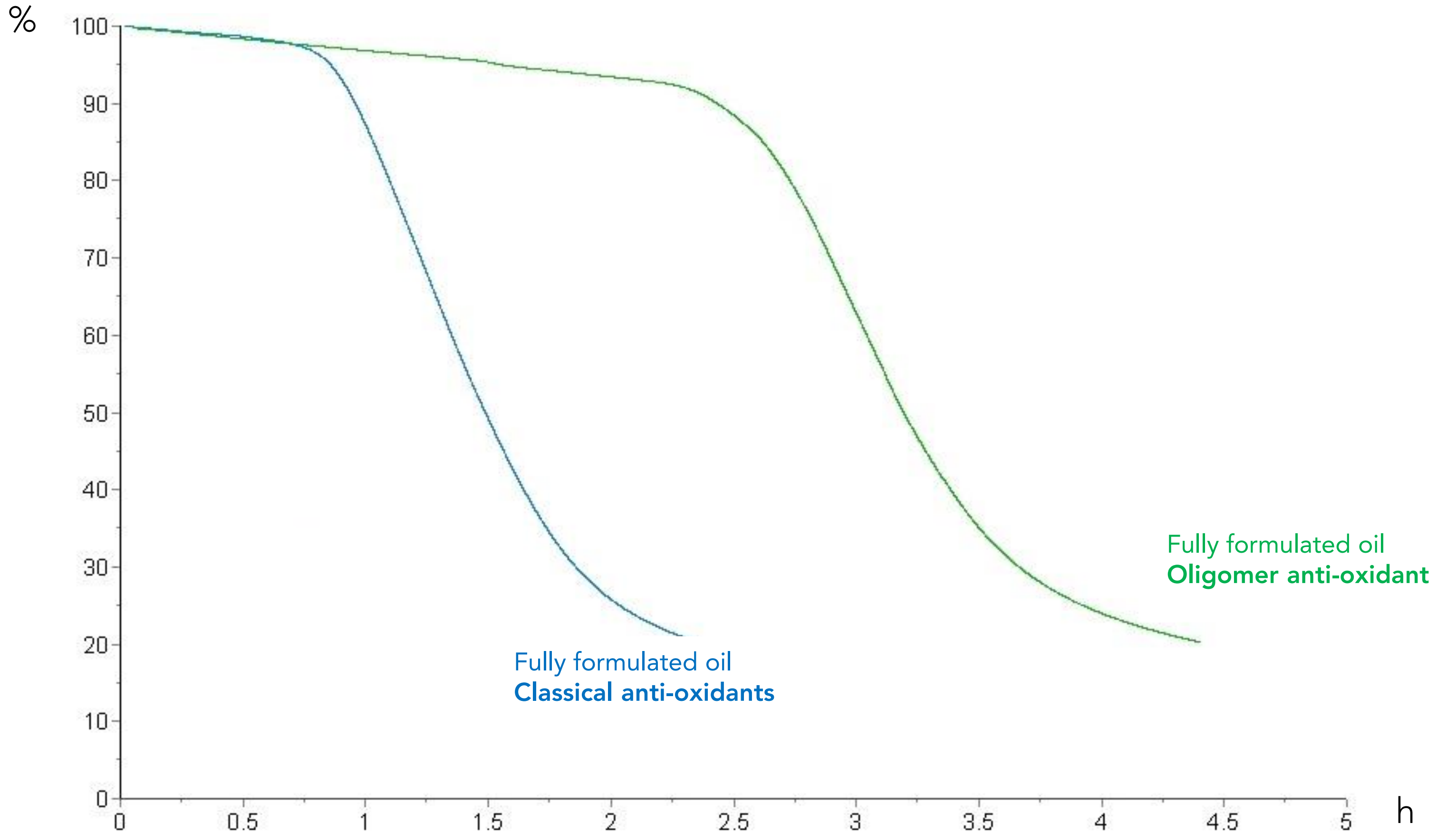
Combining branched neopolyol ester technology with oligomer antioxidant system (and suitable metal deactivator chemistry will maximize)

- *Resistance to thermo-oxidation;*
- *Cleanliness;*
- *Lifetime.*

	HT chain oil classical AO system	HT chain oil oligomer AO
KV40 – mm^2/s	227	257
KV100 – mm^2/s	19.6	20.9
COC - Celsius	317	314
Evaporation 6 h - 200°C - %	0.35	0.40

Resistance to oxidation and lifetime

Thermogravimetric analysis - O_2 – 250C



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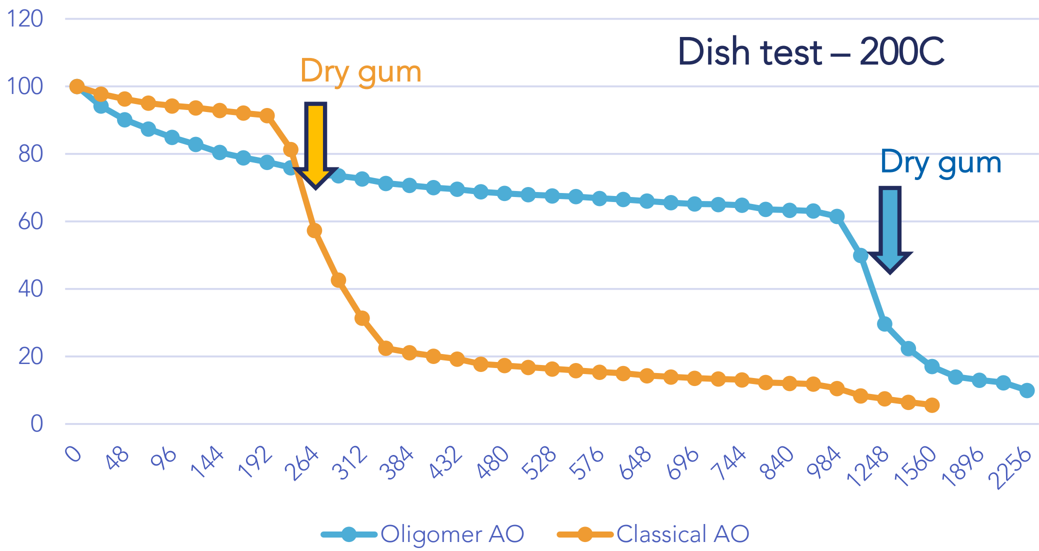
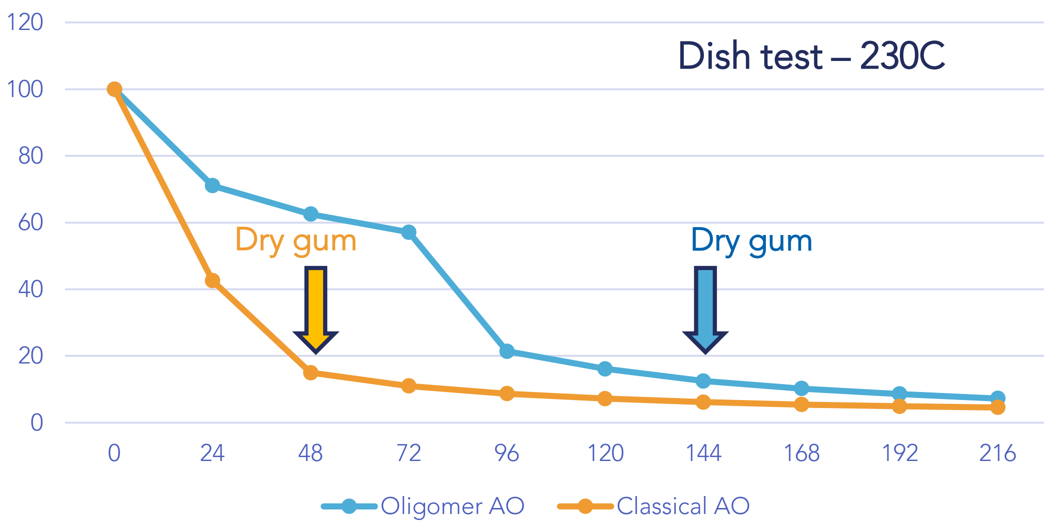
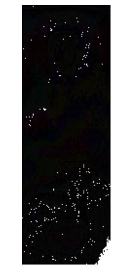
Evaporation, residue formation





	Fully formulated Classical anti-oxidant	Fully formulated Oligomer antioxidant
GFC Lu -27-A-13, Micro -Coking Test, 230 -280°C		
Deposit temperature	>280	>280
Average merit	10	10
		
GFC Lu -27-A-13, Micro -Coking Test, 250 -300°C		
Deposit temperature	< 250	266
Average merit	8.0	8.7
		
GFC Lu -27-A-13, Micro -Coking Test, 280 -330°C		
Deposit temperature	< 250	<280
Average merit	5.1	6.2
		

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Conclusion

Conclusion

- Specific antioxidant systems, deriving from oligomerized classical antioxidants, have been developed for the needs of the aviation industry

- Such a technolgy delivers outstanding performance in neopolyol esters, and is extended to high temperature lubricants such as chain oils

- Lubricants using this technology deliver extended lifetime, low volatility, improved fire safety and deposit control in temperatures exceeding 300C.

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Solutions ahead

THANK YOU


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