SAE 2010
Alternate Refrigerant & System Efficiency Symposium
July 2010, Scottsdale Arizona.

Dr Liz Dixon
Shrieve Chemical Products

Results of Shrieve Evaluations of 1234yf Refrigerant on Mobile A/C Lubricant Performance and System Chemistry

Content

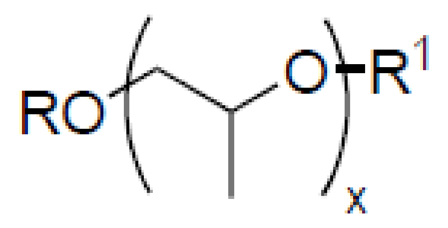
1. Review of MAC lubricant specifications - properties influenced by refrigerant change to 1234yf, & proposals on achievable performance specifications for 1234yf lubricants.

2. Summary of primary factors influencing 1234yf lubricant design and selection.

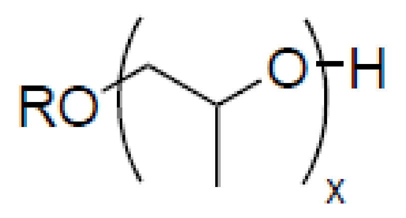
3. Stability / miscibility technical considerations for 1234yf lubricants.

4. One-product-fits-all viability (electrics, 1234yf & r134a).

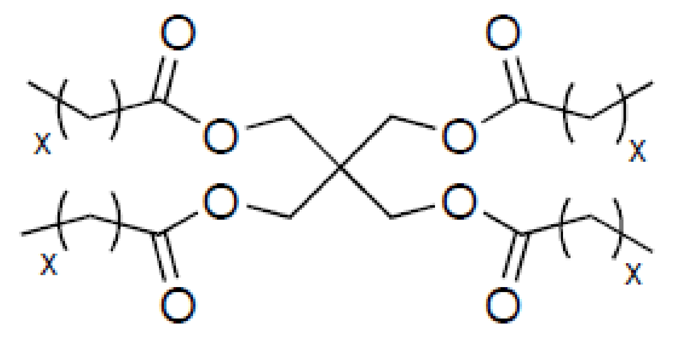
R134a Lubricant
Common Chemical Types



Dicapped PAG



Single End-Capped PAG



POE

Typical Mobile A/C PAG Lubricant (VG46) Spec.

Specification Item	Units	Method	Typical R134a	Typical 1234yf
Viscosity at 40°C (cSt)	cSt	ASTM D445	46 +/- 10%	44.0 – 56.0
Viscosity at 100°C (cSt)	cSt	ASTM D445	9.5 – 12.5	Tighter spec re. miscibility in 1234yf
Viscosity Index		ASTM D2270	>175	>190
Colour	Gardner	ASTM D1500	<1	<1
Flash point (COC)	ºC	ASTM D92	150-175 min	190
Pour point	ºC	ASTM D97	-30 max	-30 max
Specific Gravity (20°C)	Kg/m3	ASTM D1298	0.950 – 1.10	0.950 – 1.10
Capping Efficiency	%	ASTM E326	80- 90	80 -90
Total Acid Number	mgKOH/g	ASTM D974	0.1 -0.5	0.1 max
Water content	ppm	ASTM E284	500	500 max
Critical Solution Temp. (3, 10 wt% lubricant)	ºC	Ashrae 86	3wt% : 55-60 10wt% : 50-55	3wt% : 30 min 10wt% : 20 min
Sealed Tube Stability		Ashrae 97	Fe :3, Cu :2, Al : 2 <0.5% R134a decomp. TAN typical (PAG) <0.1	Fe :2, Cu :1, Al : 1 <0.5% 1234yf decomp. TAN 0.35/0.5 max (300/2000ppm H_2O)
Wear Performance		OEM Specific	-	-
Hybrid / Electric related :				
Total Acid Number	mgKOH/g	ASTM D974	<0.03	<0.03
Water content	ppm	ASTM E284	<300	<300
Ion content	ppm	ICP	<30	<30
Electrical Resistivity	Ohm cm	IEC 247	$> 10^{10}$	$> 10^{10}$
Breakdown Voltage	kV	IEC 156	< 35	< 35

Main Considerations for 1234yf lubricant design

- Chemical stability (thermal, oxidative, hydrolytic variables?)
- Refrigerant / lubricant miscibility & impact on viscometrics
- Electrical insulation properties
- MAC lubricant historical trends – applicability in current R134a systems

Refrigerant Stabilities

- R134a : 1,1,1,2-tetrafluoroethane CFH_2CF_3

- 1234yf : 2,3,3,3,-tetrafluoroprop-1-ene $CF_3CF=CH_2$

- Excellent environmental properties, low toxicity, similar system performance to R-134a, mild flammability .

- Atmospheric breakdown products are essentially the same.

- Reactive chemistries in contact with a/c system components may vary.

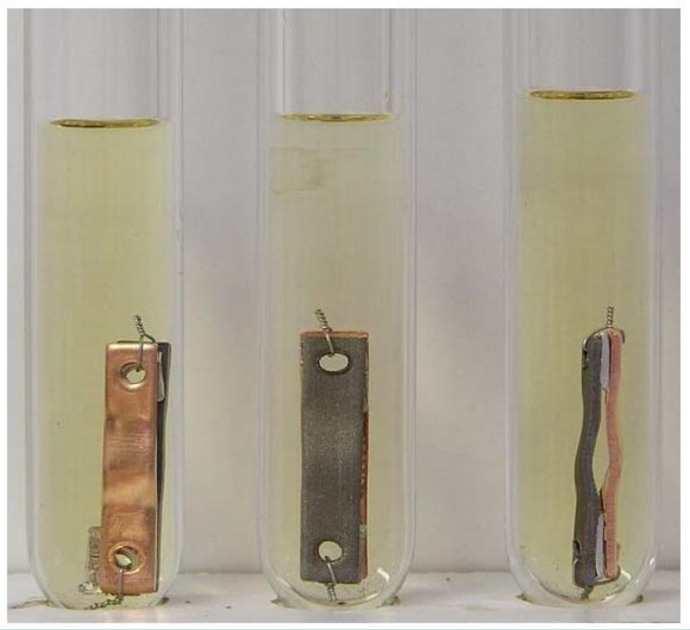
Lubricant Stabilities

- Lubricant reactive chemistries observed to differ with 1234yf compared to R134a (both PAG & POE) :

ASHRAE 97, 1234yf, 14day, 175°C, 1000ppm H_2O :

Market #1 OEM validated
Dicapped PAG

TAN **<u>1.25</u>** mgKOH/g, $[X^-]$ 105 ppm
(vs <0.03 mgKOH/g, r134a condition)



Market #2 OEM validated
Dicapped PAG

TAN <u>0.18</u> mgKOH/g, $[X^-]$ 103 ppm
(vs <0.03 mgKOH/g, r134a condition)

Lubricant Stabilities

ASHRAE 97, 1234yf, 14day, 175°C, 1000ppm H_2O :

Market #1 OEM validated
Single endcapped r134a PAG

TAN <u>0.19</u> mgKOH/g, [X^-] 110 ppm
(vs <0.03 mgKOH/g, r134a condition)

50/50 wt/wt #1 OEM validated
dicapped r134a PAG / VG46 POE.

TAN **<u>1.80</u>** mgKOH/g, [X^-] 36 ppm
(vs 0.3 - 0.6 mgKOH/g, r134a condition)

Lubricant Stabilities in 1234yf

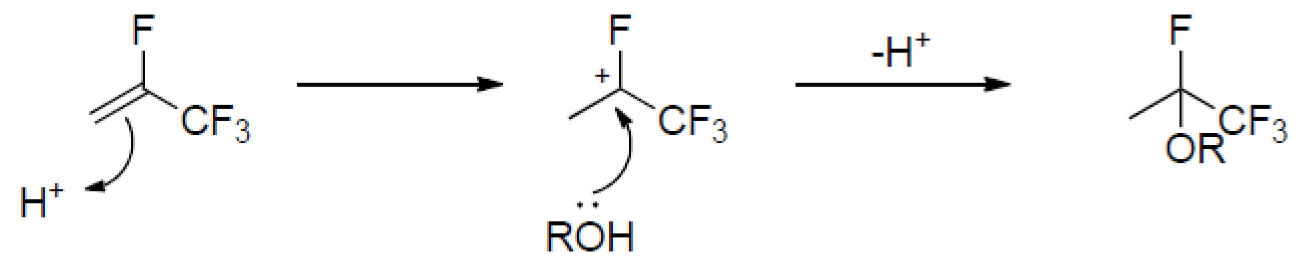
- Lubricant stability in 1234yf varies significantly between PAG types / formulations – not typically seen with r134a.

- Lubricant stability in 1234yf varies between PAG & POE – more than previously seen with r134a.

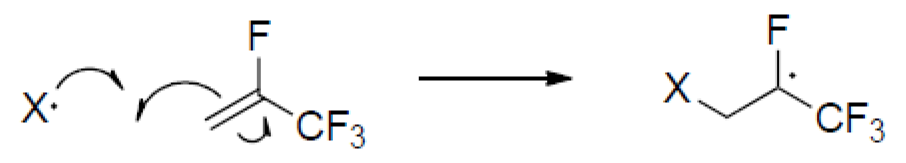
- Chemical stability spec widening required for 1234yf lubricants?

Possible mechanisms of chemical instability in 1234yf

1. Polar Chemistry : Requires acid catalysis – unlikely mechanism



2. Radical Chemistry : Requires source of initiator radical – highly likely



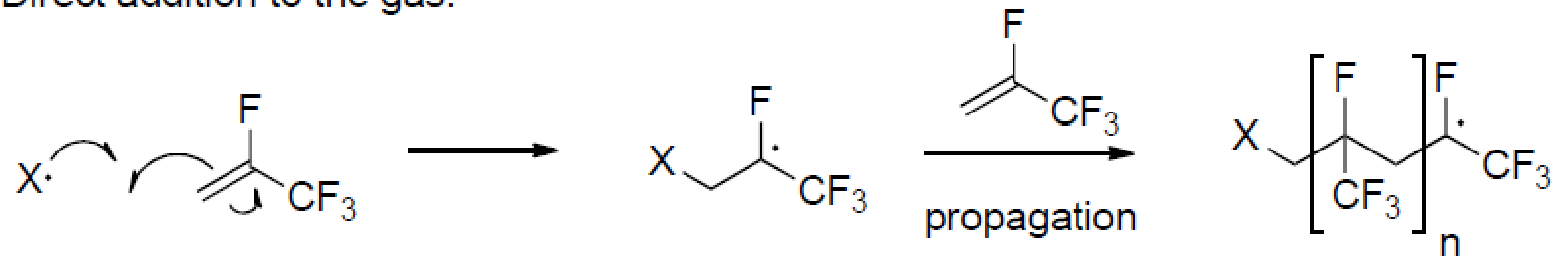
“Semi-stable” radical

Conclusion :

– Relationship between source of initiator radicals & stability of lubricant in 1234yf

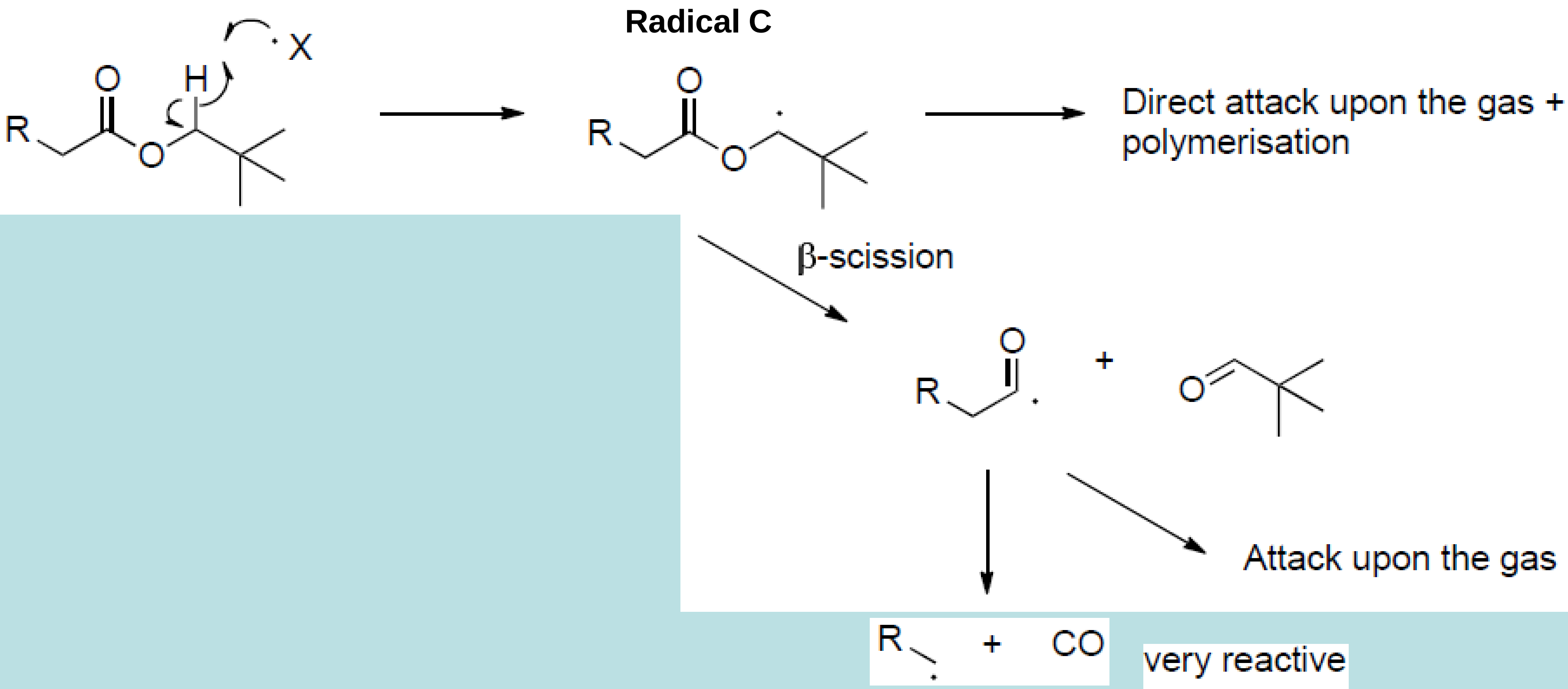
Possible Radical Pathways

Direct addition to the gas:



propagation

Abstraction of H· from POE:



Radical C

Direct attack upon the gas + polymerisation

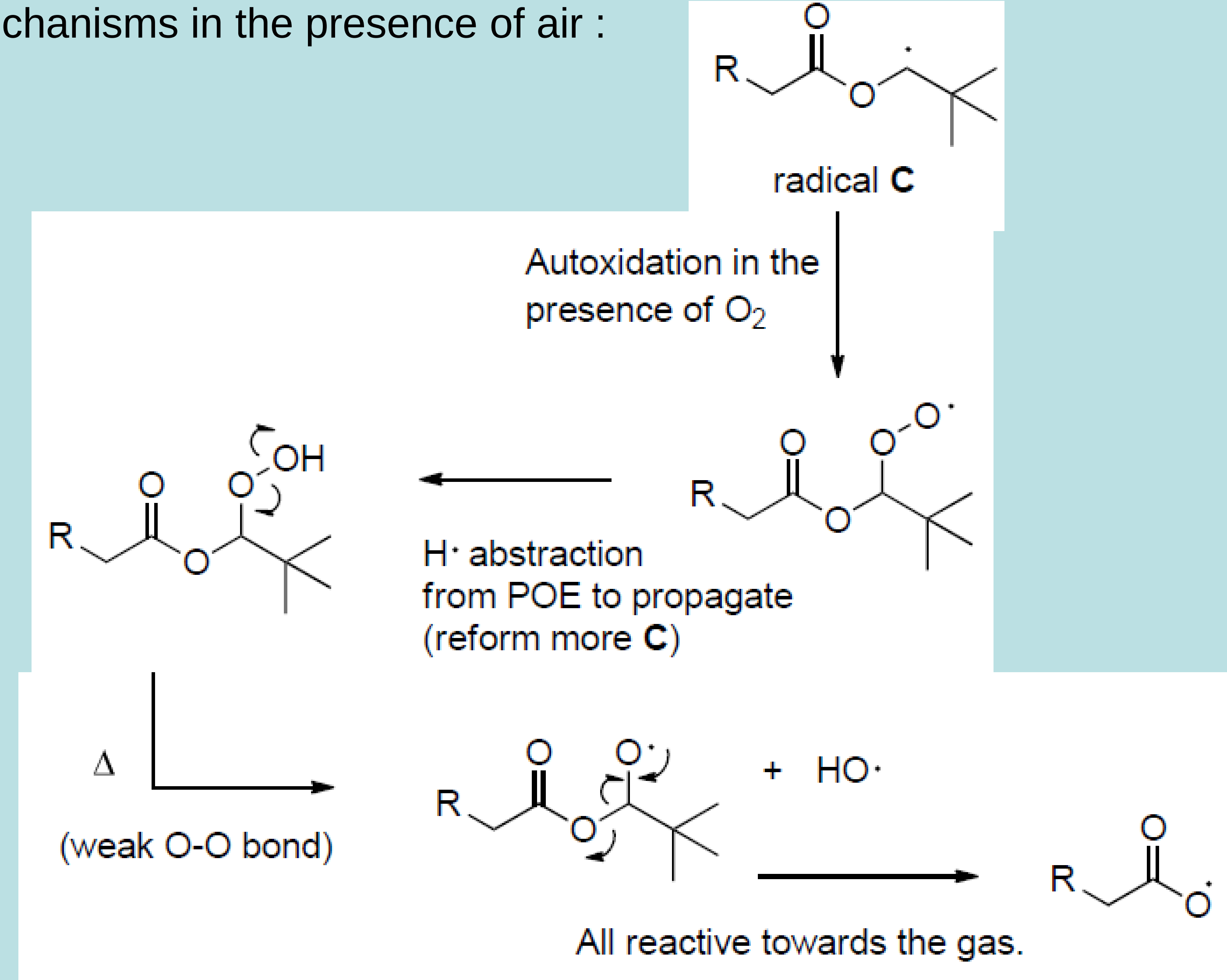
β-scission

Attack upon the gas

very reactive

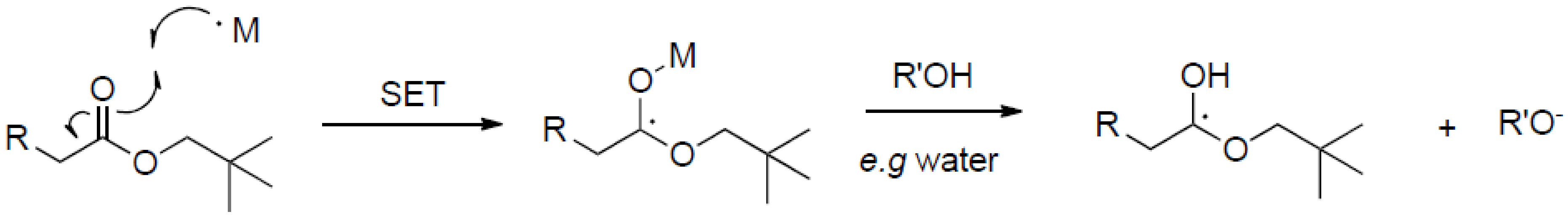
Possible Radical Pathways

Mechanisms in the presence of air :



Likely cause of increasing TAN

Likely Radical Sources



POE

ketyl radical **A**

ketyl radical **B**

<u>Factors accelerating Radical formation</u> :

Source of single electron transfer from M· - Fe^{2+}, particularly alkali metal in PAGs.

Ester functionalities (eg. POE lubricant type, ester containing additisation).

Hydroxyl functionalities (H_2O or single end-capped PAG lubricant type) .

Radical attack on 1234yf results in various chemical degradation mechanisms.

Allyl unsaturation in PAG will also accelerate degradation.

Radical pathways differ in air (variable colour / TAN changes according to additisation).

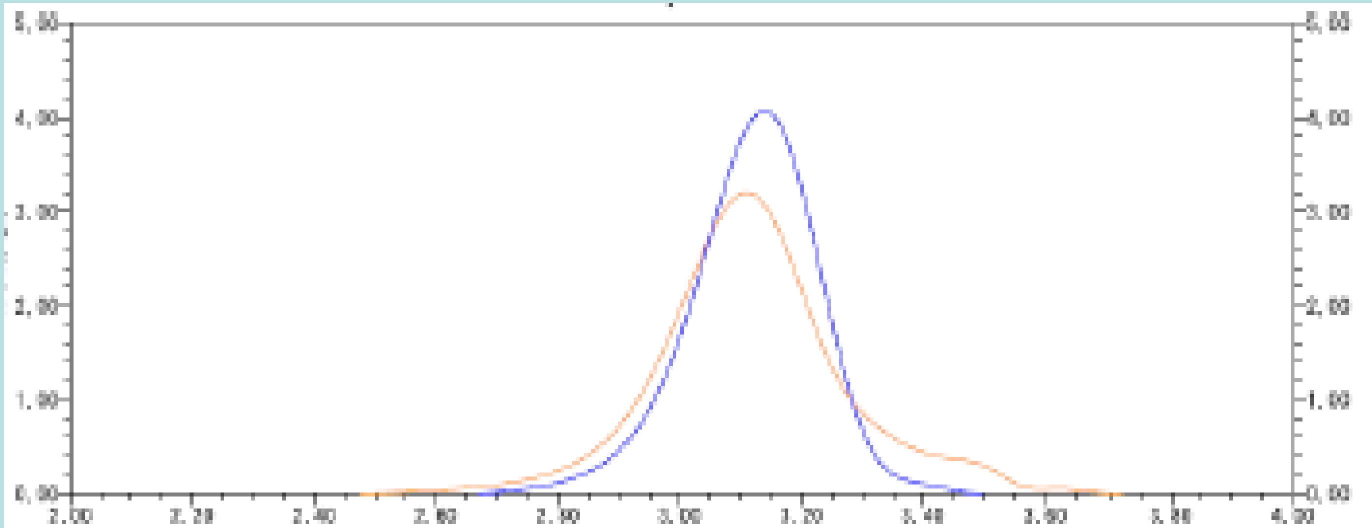
Lubricant Stabilities – effect of high mol.wt PAG

ASHRAE 97, 1234yf : lubricant (1:1), 14day, 175°C, 1000ppm H_2O, Cu / Al/ Fe :

TAN 0.08 mgKOH/g
Colour 2.0 Gdr

TAN 0.34 mgKOH/g
Colour 4.0 Gdr

GPC mol.wt distribution of VG46 blended dicapped PAG vs direct reacted :



Reactive Chemistry Solutions

Minimise utilisation of ester containing basefluid / additive chemistries.

Minimise presence of water / air to reduce radical formation and further auto-oxidation.

Reduce hydroxyl functionalities (dicapped PAGs with maximised capping efficiencies).

Reduce PAG allyl unsaturation (direct reacted to correct PAG viscosity).

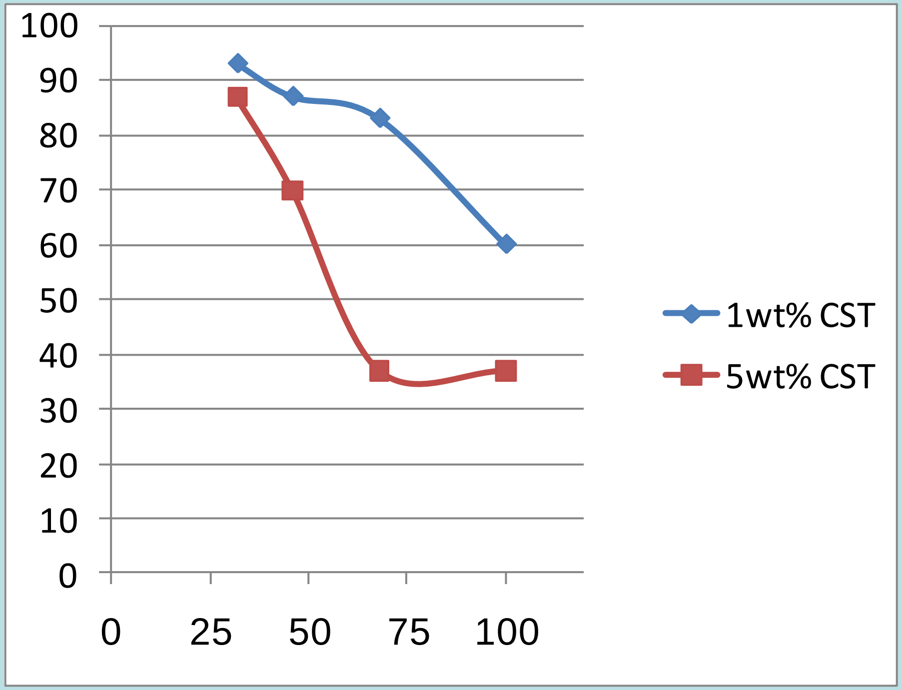
Optimise antioxidant additisation synergies.

Optimisation of free radical scavenging additisation.

Refrigerant / lubricant miscibility & impact on viscometrics

Typical R134a dicapped PAG viscosity vs CST relationship :

Viscosity Grade , cSt (40ºC)	Wt% lubricant	Upper Critical Solution Temperature
32	1	93
32	5	87
46	1	87
46	5	70
68	1	83
68	5	37
100	1	60
100	5	37



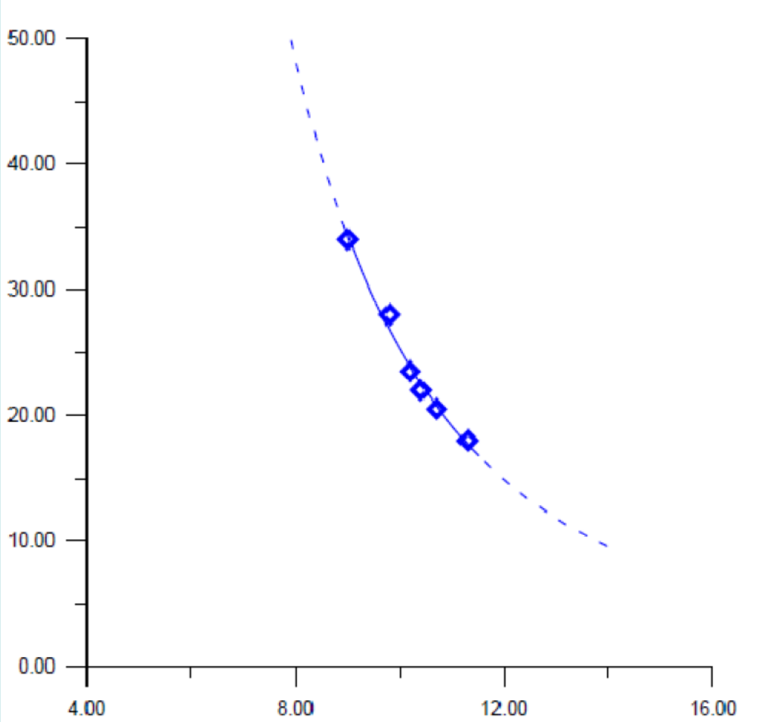
V40 range covered 32 – 68cSt.
Shift of 10º in CST over 36cSt, approx.
1ºC per 3.6cSt at 40ºC.

Refrigerant / lubricant miscibility & impact on viscometrics

Typical 1234yf VG46 dicapped PAG viscosity vs CST relationship :

Viscosity , cSt (100ºC)	Upper Critical Solution Temperature at 20wt% lubricant
9.0	34.0
9.8	28.0
10.2	23.5
10.4	22.0
10.7	20.5
11.3	18.0

20wt% CST



Viscosity (cSt) at 100ºC

V40 range covered 44 – 58cSt.
Shift of 16º in CST over 14cSt, approx.
1ºC per cSt at 40ºC.

Miscibility and Viscometric Conclusions :

Greater dependence of 1234yf miscibility on dicapped PAG viscosity.

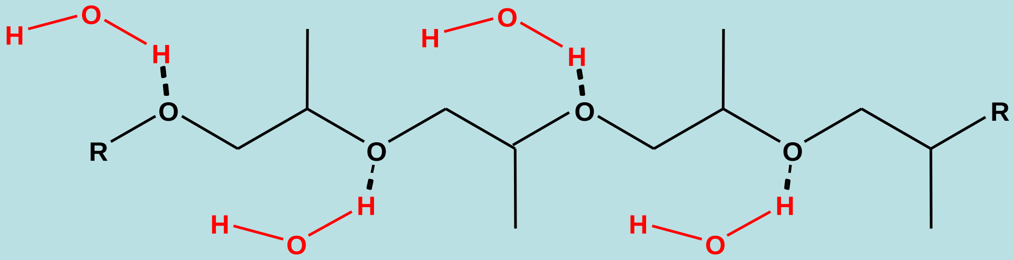
Tighter tolerances required on viscometrics within traditional VG46 range (+/- 10%).

1234yf Electrics – technical considerations :

Impact of lubricant hygroscopicity

Electrical properties of non-POE lubricants

Electrical Properties – Water Absorption



- Water is “hydrogen bonded” to ether functionalities of the PAG - does not exist freely within the system. Consequently most undesirable effects of high water absorption are not observed.

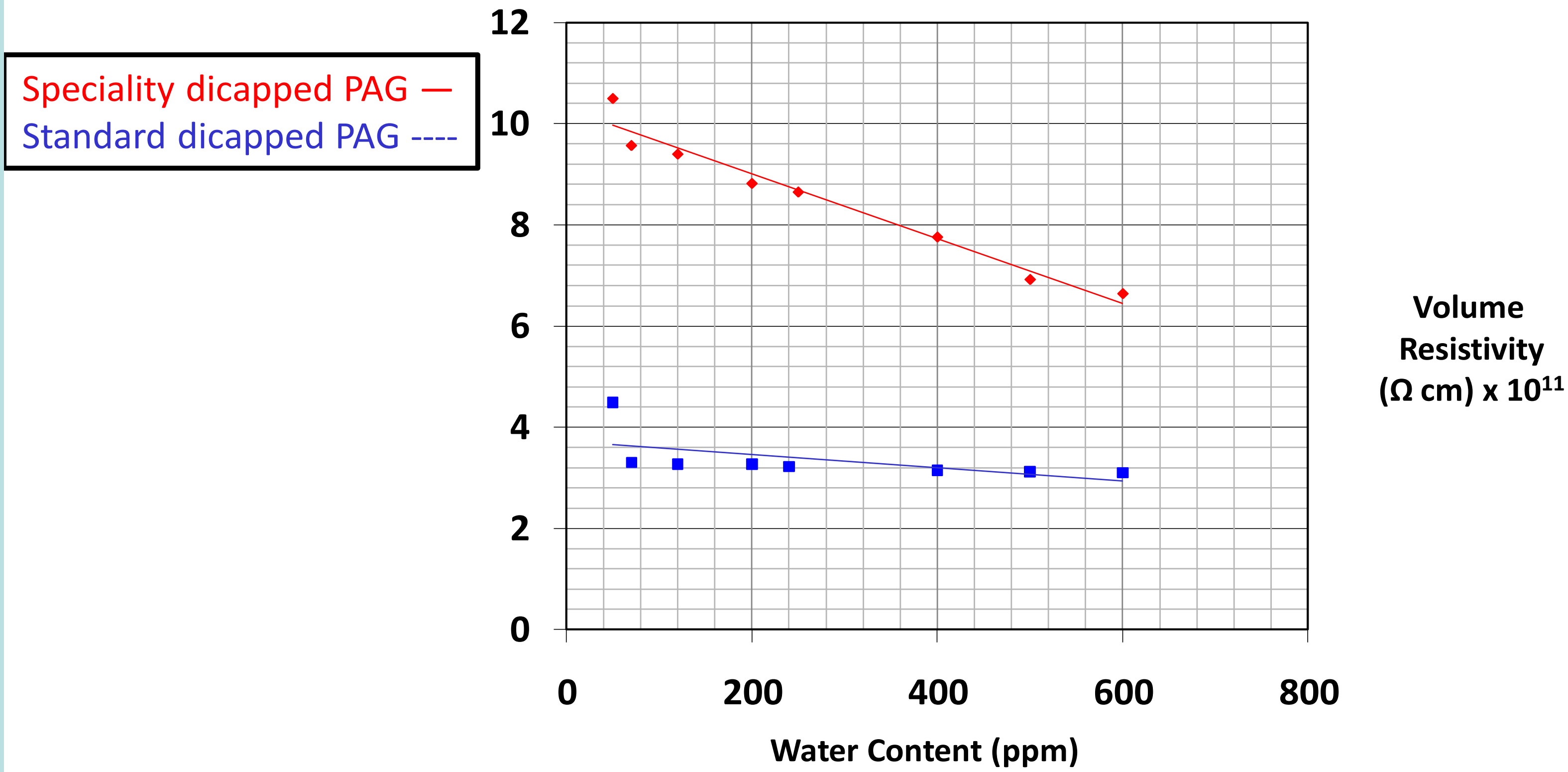
- POE molecules typically contain one ester functionality - opportunity for hydrogen bonding is limited so water freely exists in POE.

- POE is highly reactive with water, generating acidic species.

- Chemical instability is common in POE lubricants, therefore very low water specifications must be employed for POE.

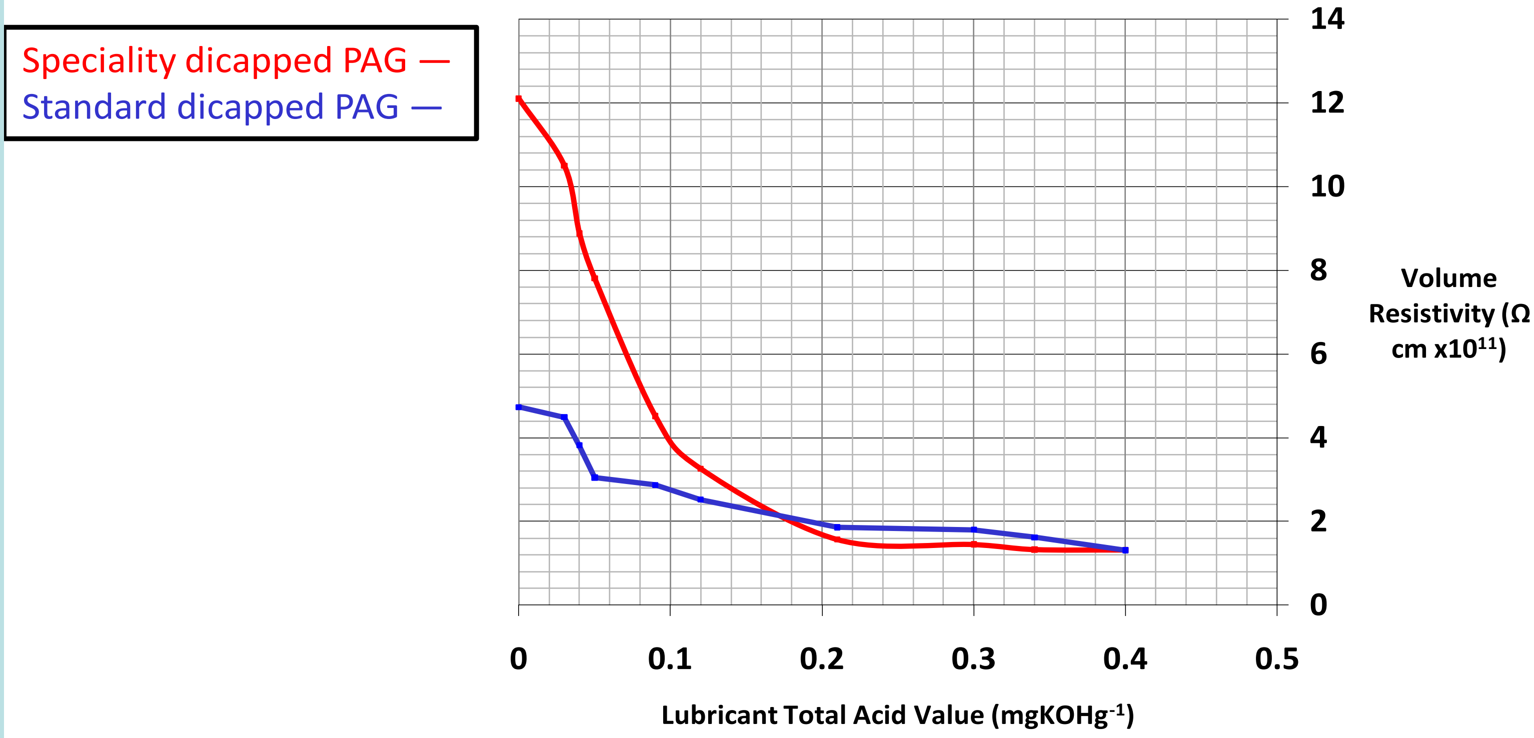
- Industry water spec standard for POE is <50ppm, industry standard for PAG is <500pm

Volume Resistivity (Ω cm) as a function of Moisture Content : Dicapped PAGs



Total Acid Value constant for all samples at 0.03 mgKOH/g
Alkali metal ions constant for all samples at 30ppm

Volume Resistivity (Ω cm) as a function of Total Acid Value : Dicapped PAGs



Water content constant for all samples at 50ppm
Alkali metal ions constant for all samples at 30ppm

Lubricant Type	Volume Resistivity (ohm cm)	Dielectric Strength (kV)
VG 46 Electric POE	1.8×10^{14}	44
Specification optimised dicapped PAG	1.06×10^{12}	38
Standard dicapped PAG	8.7×10^{11}	38

Summary :

Speciality double end-capped PAG likeliest technical choice for 1234yf.

- Control of basestock type, viscosity and mol.wt distribution, for optimum 1234yf miscibility.
- Additisation optimisation for chemical stability control.

Future 1234yf & 134a electrics may utilise same PAG.

-Accurate control of PAG water, TAN & ion specification required to fulfill electrical properties.

-Water ingress during system life will increase conductance but can be controlled by additisation technologies.