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"Results of Shrieve evaluations of R1234yf refrigerant on mobile A/C lubricant performance and system chemistry"

Content

- Lubricant properties which are influenced by refrigerant change to R1234yf.
- Proposals on achievable performance specifications for R1234yf lubricants.

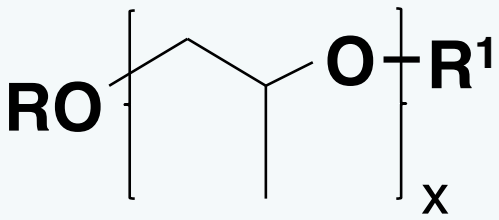
1. Summary of primary factors influencing R1234yf lubricant design and selection.

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

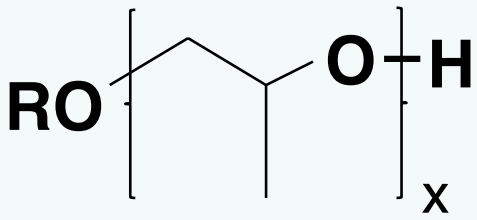
3. ‘One-product-fits-all’ viability; (electrics, R1234yf and R134a).

R134a lubricant – common chemical types

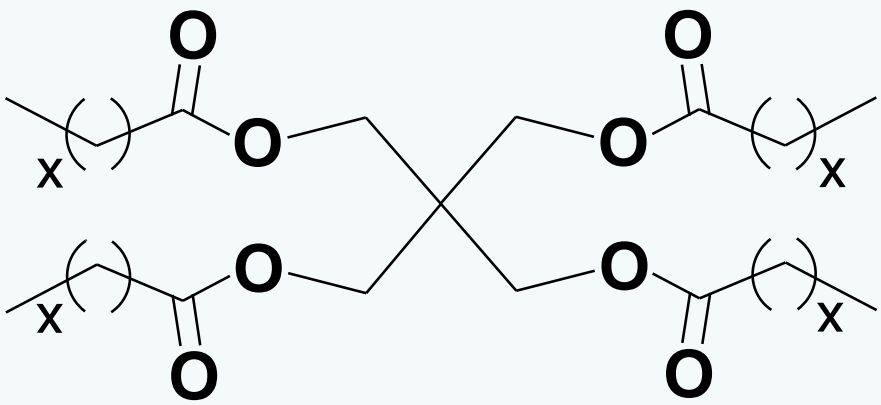
Dicapped PAG



Single End-Capped PAG



POE



Typical Mobile A/C PAG lubricant (VG46) spec.

Specification Item	Units	Method	Typical R134a	Typical R1234yf
Viscosity at 40°C (cSt)	cSt	ASTM D445	46 +/- 10%	42.0 – 45.0
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)	°C	ASTM D92	150 - 175 min	190
Pour point	°C	ASTM D97	-30 max	-30 max
Specific Gravity (20°C)	Kg/m^3	ASTM D1298	0.950 – 1.10	0.950 – 1.10
Capping Efficiency	%	ASTM E326	80 - 90	> 90
Total Acid Number	mgKOH/g	ASTM D974	0.1 - 0.5	0.05 max
Water content	ppm	ASTM E284	500	300 max
Critical Solution Temp. (3, 10 wt% lubricant)	°C	Ashrae 86	3wt% : 55-60 10wt% : 50-55	2wt% : 52 min 10wt% : 23 min
Sealed Tube Stability		Ashrae 97	Fe: 2, Cu: 2, Al: 2 <0.5% R134a decomp. TAN typical (PAG) <0.1	Fe: 2, Cu: 2, Al: 2 HF limits TAN 0.30 / 0.80 max (350/2000ppm 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 - R1234yf lubricant design

- Chemical stability;
  (thermal, oxidative, hydrolytic variables?)
- Refrigerant/lubricant miscibility & impact on viscometrics

(Draft VDA lubricating oil spec reflecting primary issues)

- Electrical insulation properties
- MAC lubricant historical trends – applicability in current R134a systems

Refrigerant Stabilities

- **R1234yf:** 2,3,3,3,-tetrafluoroprop-1-ene $CF_3CF{=}CH_2$

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

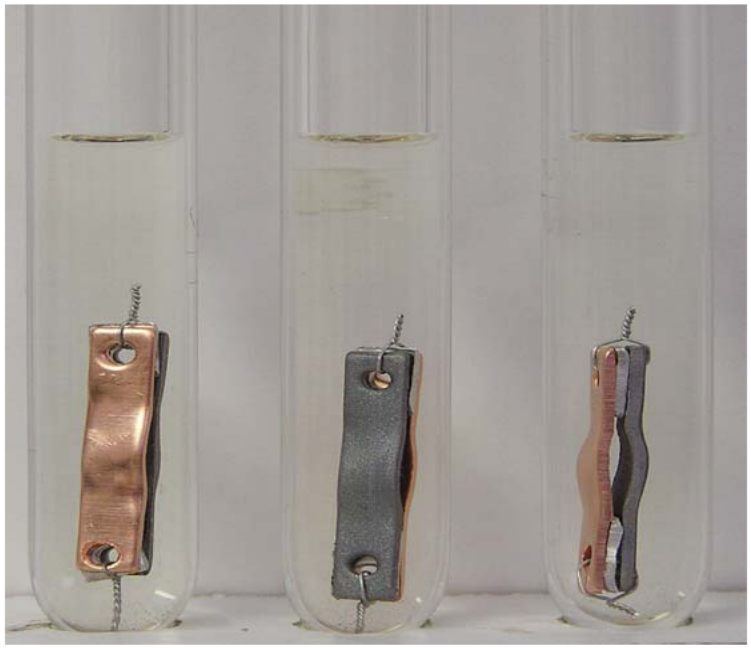
- Atmospheric breakdown products are essentially the same as R134a.

- Reactive chemistries in contact with a/c system components may vary – impacts lubricant design.

Lubricant Stabilities (1)

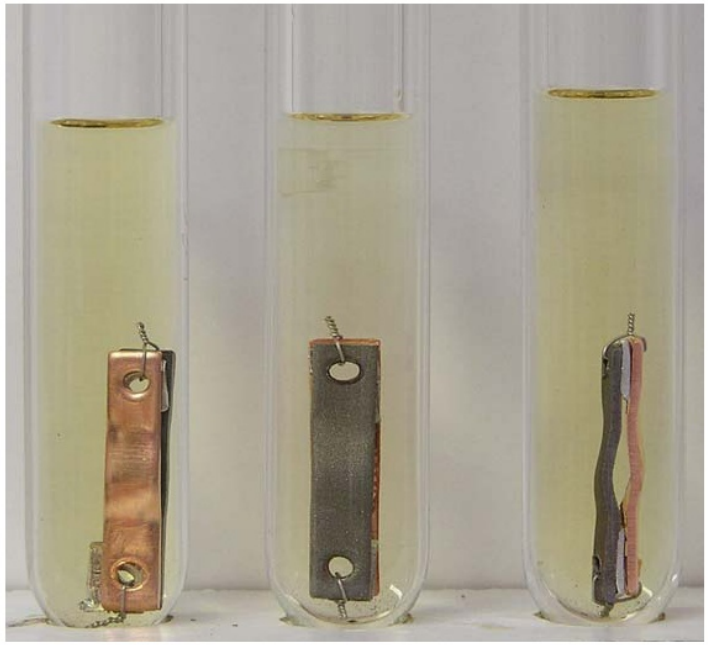
Lubricant reactive chemistries observed to differ with 1234yf compared to R134a (PAG/POE):

ASHRAE 97, R1234yf, 14day, 175°C, 1000ppm H_2O:



Market #1 OEM validated
Dicapped PAG

TAN **1.25** mgKOH/g.
(vs <0.03 mgKOH/g, R134a condition)



Market #2 OEM validated
Dicapped PAG

TAN 0.18 mgKOH/g.
(vs <0.03 mgKOH/g, R134a condition)

Lubricant Stabilities (2)

ASHRAE 97, R1234yf, 14 day, 175°C, 1000ppm H_2O:

Market #1 OEM validated
Single endcapped R134a PAG

TAN **0.19** mgKOH/g.
(vs <0.03 mgKOH/g, R134a condition)

50/50 wt/wt #1 OEM validated
dicapped R134a PAG/VG46 POE

TAN **1.80** mgKOH/g.
(vs 0.3 - 0.6 mgKOH/g, R134a condition)

Lubricant Stabilities in R1234 yf - Conclusions

- Lubricant stability in R1234yf varies significantly between PAG types/formulations – not typically seen with R134a.
- Lubricant stability in R1234yf varies between PAG & POE – more than previously seen with R134a.
- Chemical stability spec. widening required for R1234yf lubricants, & lubricant stabilisation required.

Chemical Instability in R1234yf

Factors initiating Chemical Instability :

•Source of initiator radicals (M·) resulting in attack of R1234yf double bond.

Factors accelerating Chemical Instability (radical propagation) :

•Ester functionalities (e.g. POE lubricant type, ester based additives)

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

•Radical pathways accelerated in air – exclude from system.

•Allyl unsaturation in PAG will also accelerate degradation

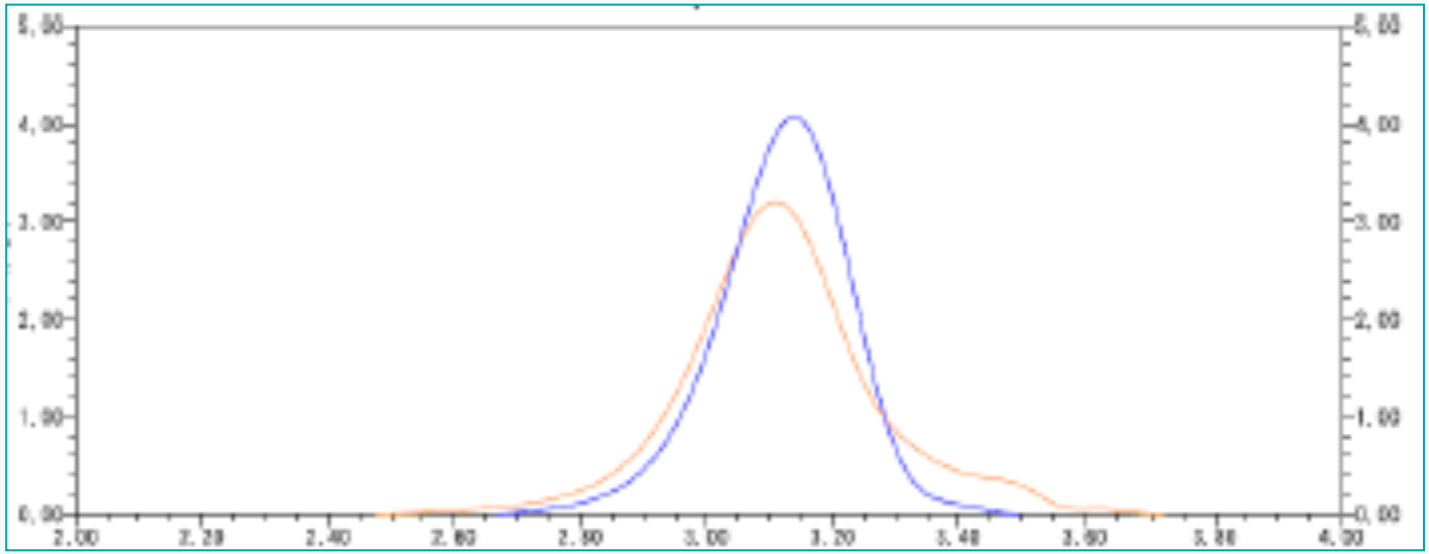
Lubricant Stabilities – effect of high mol.wt PAG

ASHRAE 97, R1234yf : lubricant (1:1), 14 day, 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 base fluid/additive chemistries
- Minimise presence of water/air to reduce radical formation and further auto-oxidation
- Reduce hydroxyl functionalities (use dicapped PAGs with maximised capping efficiencies)
- Reduce PAG allyl unsaturation (direct reacted PAG, to required viscosity)
- Optimise antioxidant additisation synergies

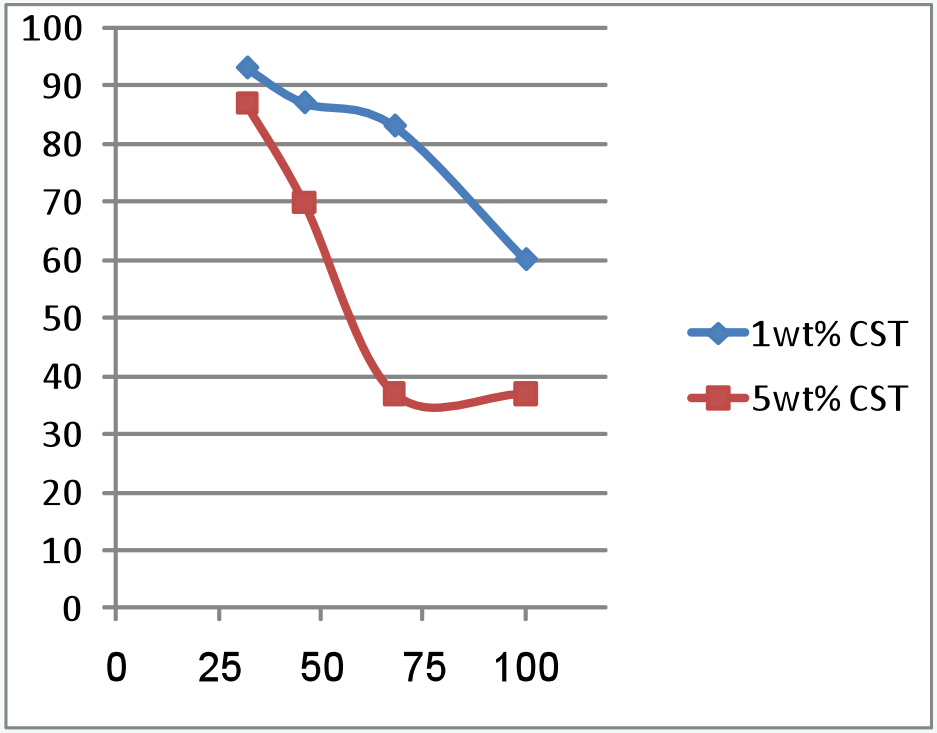
Optimisation of free radical scavenging additisation

Refrigerant/lubricant relationship

Miscibility and impact on viscometrics (1)

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 relationship

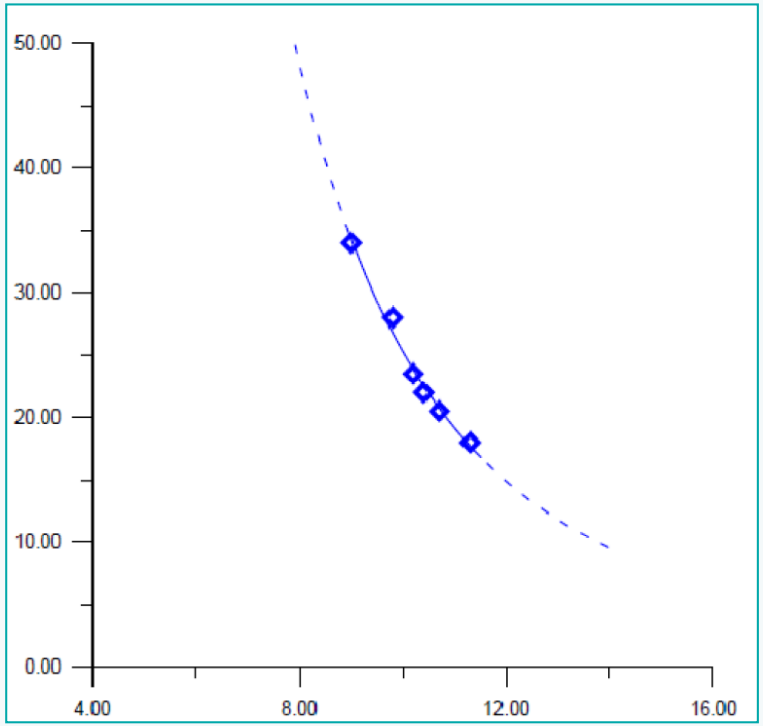
Miscibility and impact on viscometrics (2)

Typical R1234yf 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

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

20wt% CST



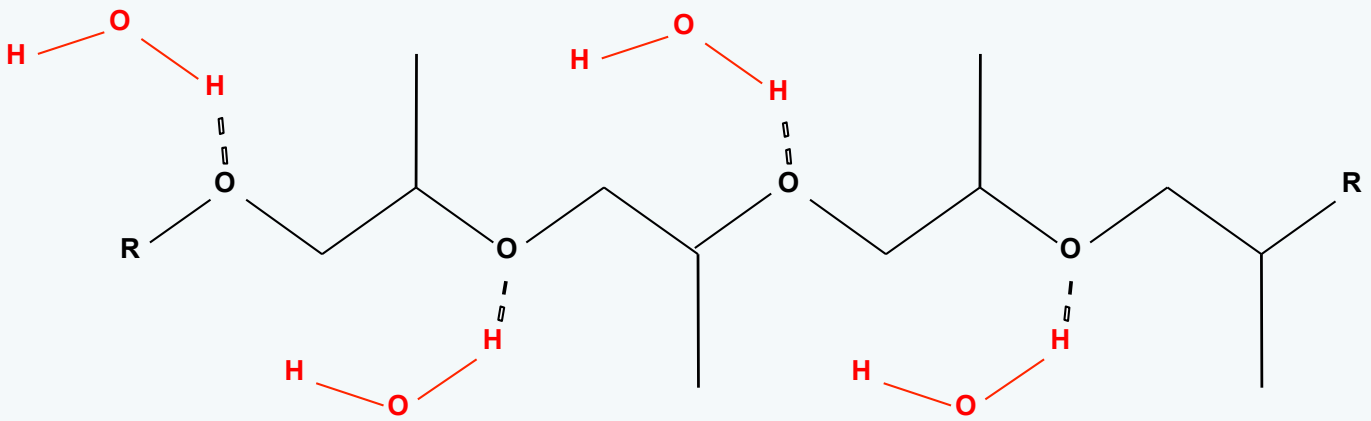
Viscosity (cSt) at 100ºC

- **Greater dependence of R1234yf miscibility on dicapped PAG viscosity.**
- **Tighter tolerances required on viscometrics within traditional VG46 range. eg. 42.0 – 45.0 cSt, compared to 41.4 – 50.6 cSt.**

1234yf Electrics - technical considerations:

- Impact of lubricant basestock on electrical resistivity
- Impact of lubricant hygroscopicity on electrical resistivity
- Impact of lubricant “impurity” on electrical resistivity

PAGs are highly hygroscopic :

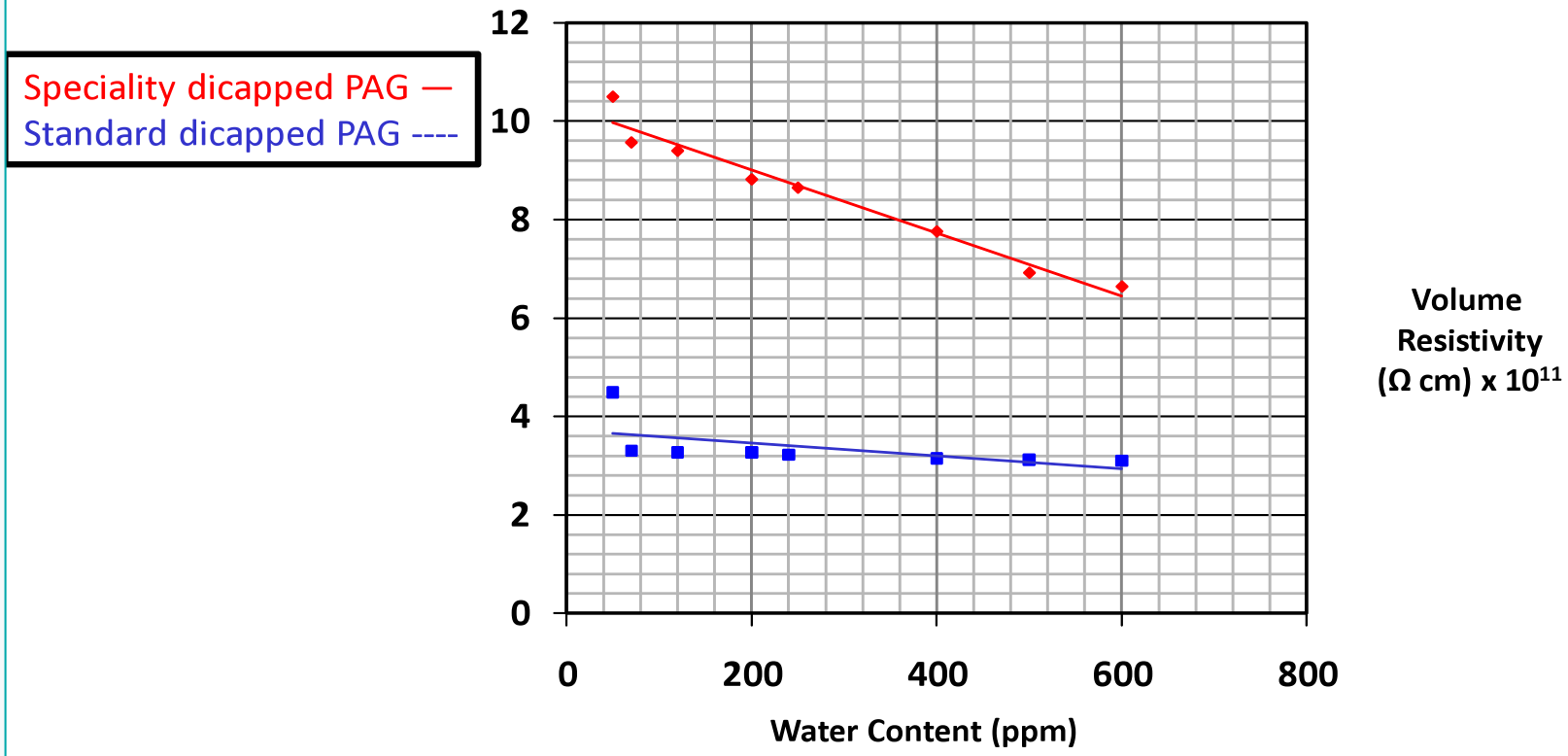


Electrical properties – Water absorbtion

- Water is “hydrogen bonded” to the PAG -: water does not exist freely within the system. Undesirable effects of high water are not observed (no corrosion, no lubricating performance reduction).
- POE molecules typically contain only ester functionality - opportunity for hydrogen bonding is limited - water freely exists in POE (corrosion, wear impact).
- POE is highly reactive with water, generating acidic species, therefore very low water specifications must be employed for POE (<50ppm typical).
- Industry standard for PAG is <500pm – is this impacting electrical property?

Electrical properties – Moisture content

Volume resistivity (Ω cm) as a function of **moisture content** (dicapped PAGs):

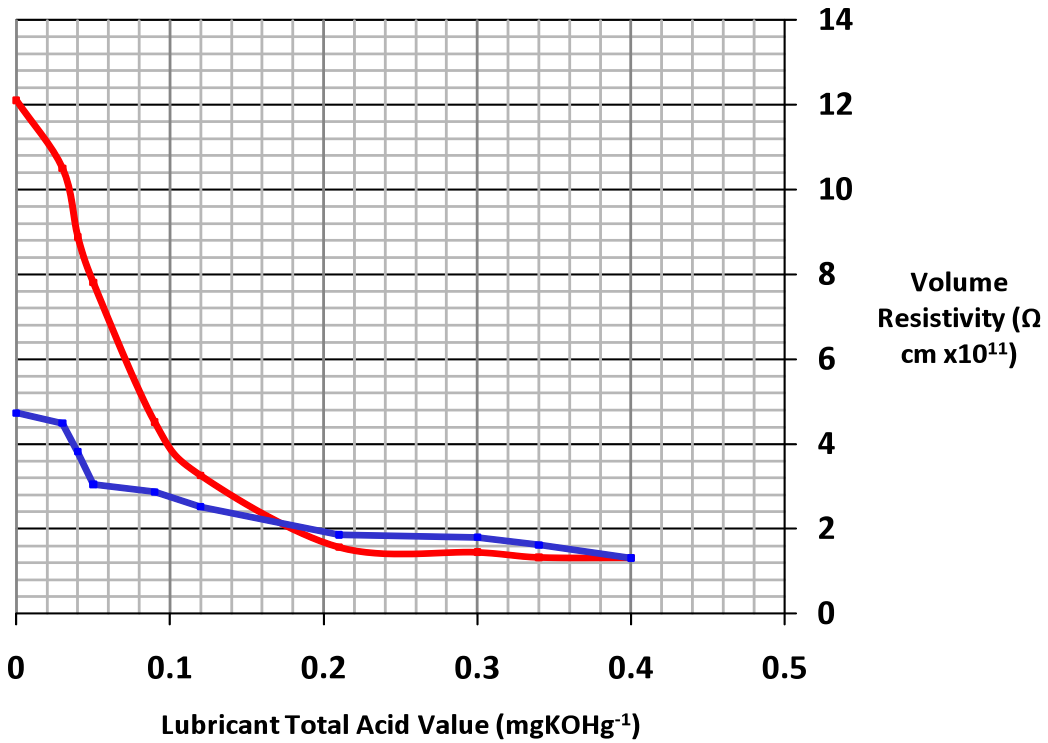


Total Acid Value constant for all samples at 0.03 mgKOH/g
Alkali metal ions constant for all samples at 30ppm

Electrical properties – Moisture content

Volume resistivity (Ω cm) as a function of **Total Acid Value** (dicapped PAGs):

Speciality dicapped PAG —
Standard dicapped PAG —



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

Electric property comparison

Lubricant Type	Volume Resistivity (ohm cm)
VG 46 Electric POE	1.8×10^{14}
Specification optimised dicapped PAG	1.1×10^{12}
Standard dicapped PAG	8.7×10^{10}

Impact of new R1234yf PAG on Servicing :

•Similarity in lubricant chemistries for R134a PAG & R1234yf PAG: no major lubricant related service issues.

•R1234yf PAG is compatible in all proportions with standard mobile a/c PAGs & POEs, and technically suitable for use in R134a.

•Some elastomer types may be unsuitable for use.

•Usual precautions regarding moisture ingress due to PAG hygoscopicity should be observed.

Summary

Speciality double end-capped PAG is the prime technical choice for R1234yf.

•Control of basestock type, viscosity and mol.wt distribution is necessary for optimum R1234yf miscibility.

•Additisation optimisation is essential for chemical stability control.

Future R1234yf & R134a electrics can utilise the same PAG.

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

•Water ingress during system lifetime will increase conductance but this can be controlled by dessicant technologies.

No significant new lubricant related servicing considerations are required.