

Development of PVE Refrigeration Lubricants for R32

July 17 2014

T. Matsumoto, M. Kaneko and Y. Kawaguchi

Idemitsu Kosan Co., Ltd.

Transition of Refrigerants and Lubricants 2

		Montreal Protocol	Kyoto Protocol
Air-Conditioner (PAC, RAC)	Ref. Oil	R22 MO	R410A PVE, POE
Vender Machine (VM)	Ref. Oil	R22 MO	R407C PVE, POE
Showcase (SC)	Ref. Oil	R22/R502 MO	R404A PVE, POE
HP-Water Heater (HPWH)	Ref. Oil		
Refrigerator	Ref. Oil	R12 MO	R134a POE
Car-A/C	Ref. Oil	R12 MO	R134a PAG

Transition of Refrigerants and Lubricants 3

		Montreal Protocol	Kyoto Protocol	
Air-Conditioner (PAC, RAC)	Ref. Oil	R22 MO	R410A PVE, POE	R32, R1234yf PVE, POE
Vender Machine (VM)	Ref. Oil	R22 MO	R407C PVE, POE	
Showcase	Ref.	R22/R502	R410A	CO₂
		R410A	R32	R1234yf
Molecular structure	CH₂F₂ / CF₃CHF₂	50 / 50	CH₂F₂	CF₃CF=CH₂
ODP	0	0	0	0
GWP	2088	675	4	4
M.W. (g/mol)	52 / 120	52	114	114
Tc (°C)	72.0	78.1	94.7	94.7
Pc (MPa)	5.0	5.8	3.4	3.4

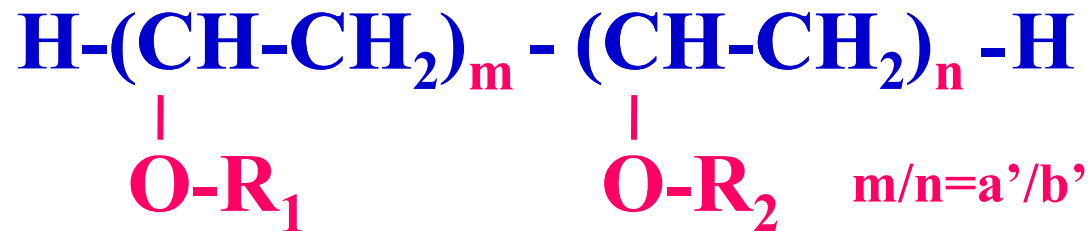
for R32

Properties of PVEs for R410A and R32

5

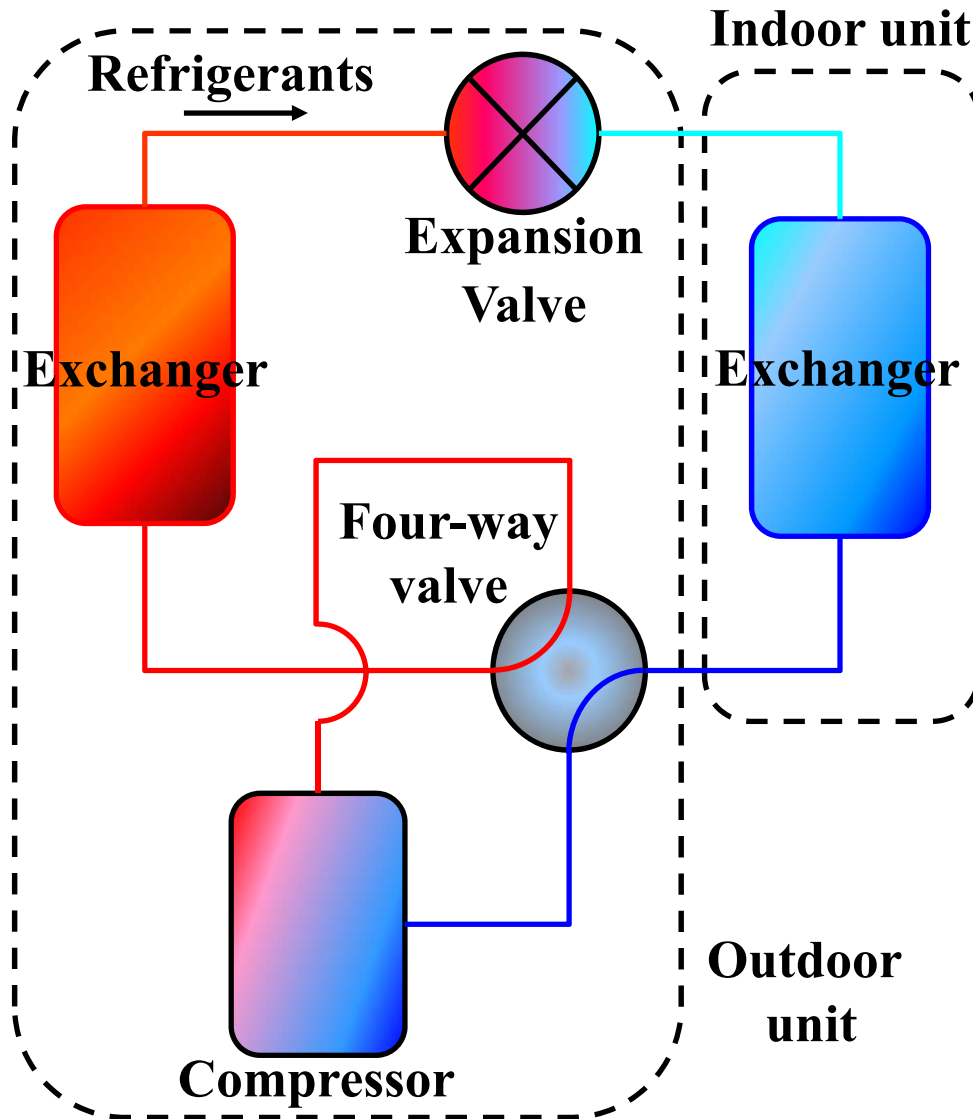
Lubricant	PVE-1A	PVE-2A	
Refrigerant	R410A	R32	
Viscosity @40°C (mm ² /s)	66.57	68.41	
Viscosity @100°C (mm ² /s)	8.037	8.316	
Viscosity Index	84	88	
Density @15°C (g/cm ³)	0.9369	0.9440	
Acid Number (mgKOH/g)	0.01>	0.01>	
Base Oil	PVE-1	PVE-2	
additive	antiwear	include	include
	antioxidant	include	include
	acid catcher	include	include

⇒ A



Chemical Structure of PVE-2 was modified PVE-1

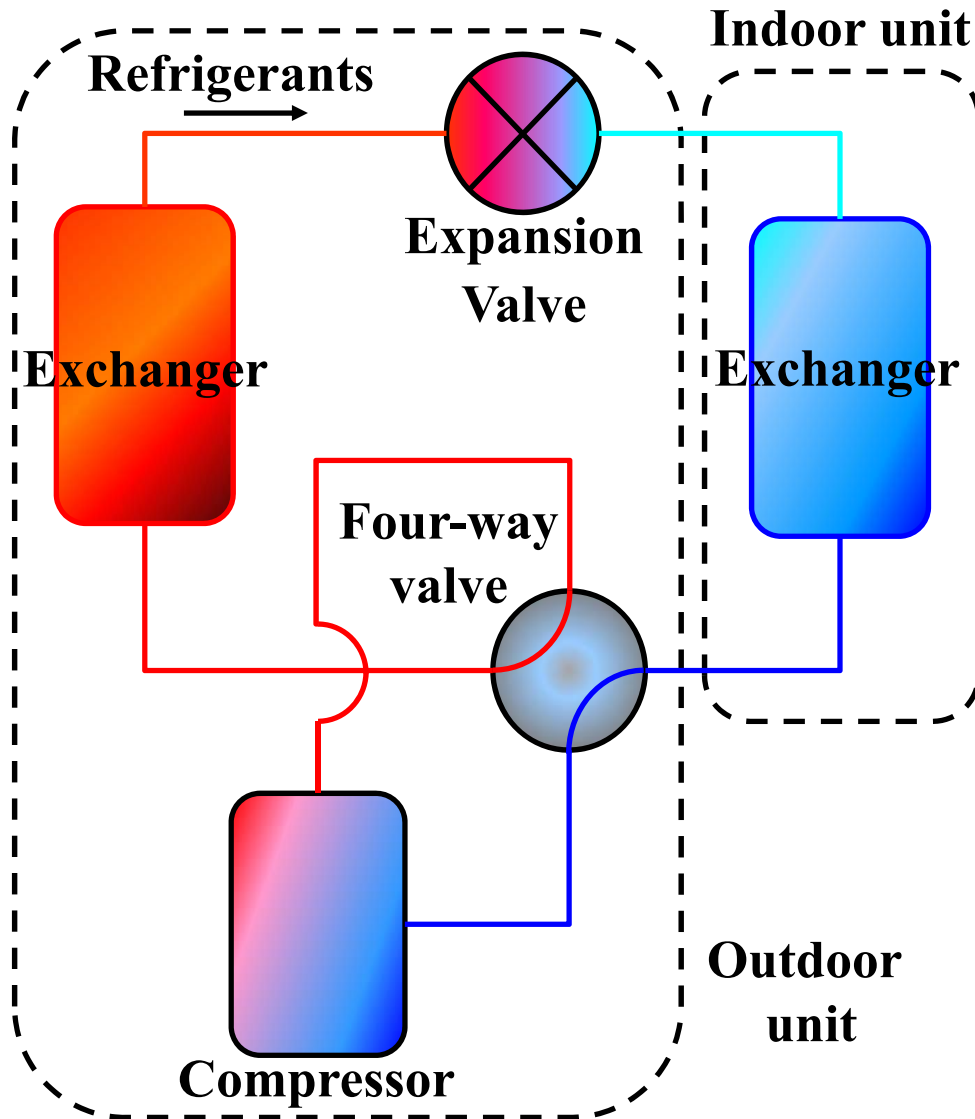
Requirements for Refrigeration Oil



1. Miscibility
2. Solubility
3. Mixture Viscosity
4. Lubricity
5. Volumetric Resistivity
6. Stability
7. Compatibility

Miscibility of PVEs for R32

7

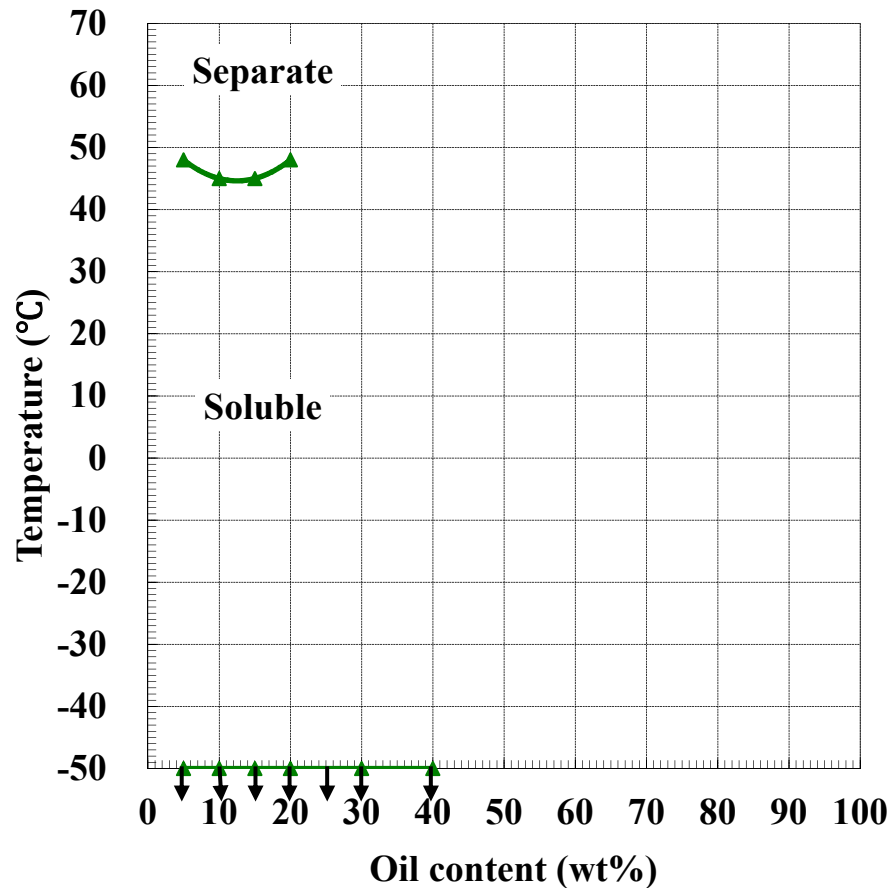


1. Miscibility
2. Solubility
3. Mixture Viscosity
4. Lubricity
5. Volumetric Resistivity
6. Stability
7. Compatibility

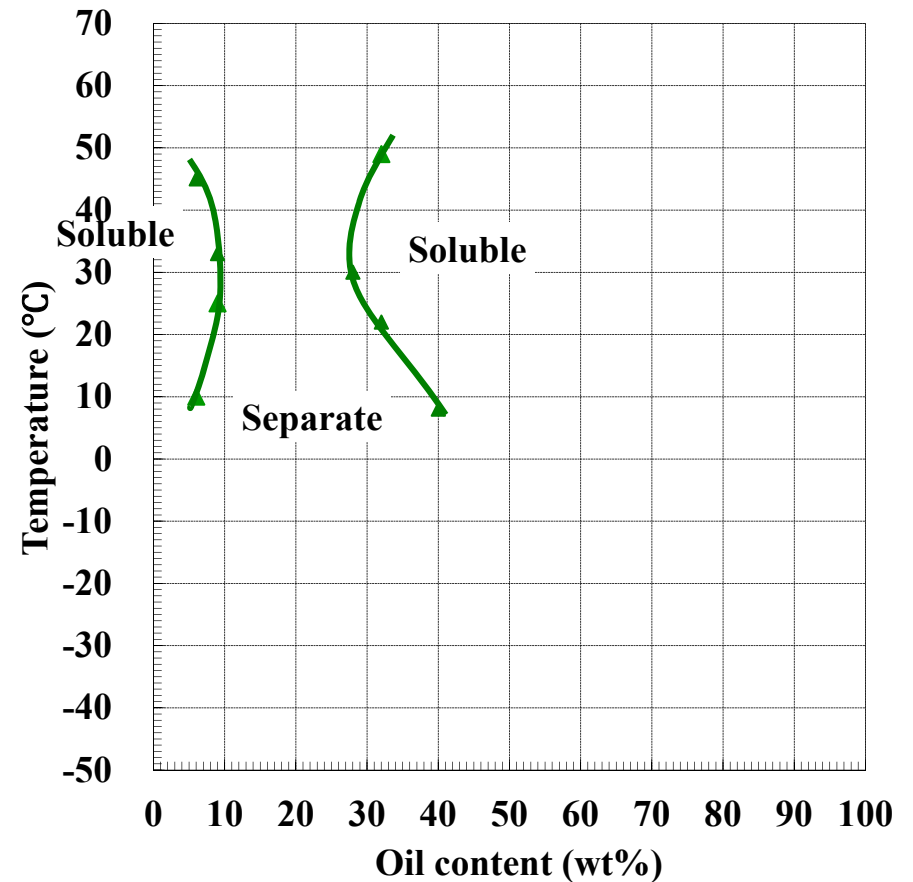
Miscibility of PVE-1A with R410A, R32

8

R410A



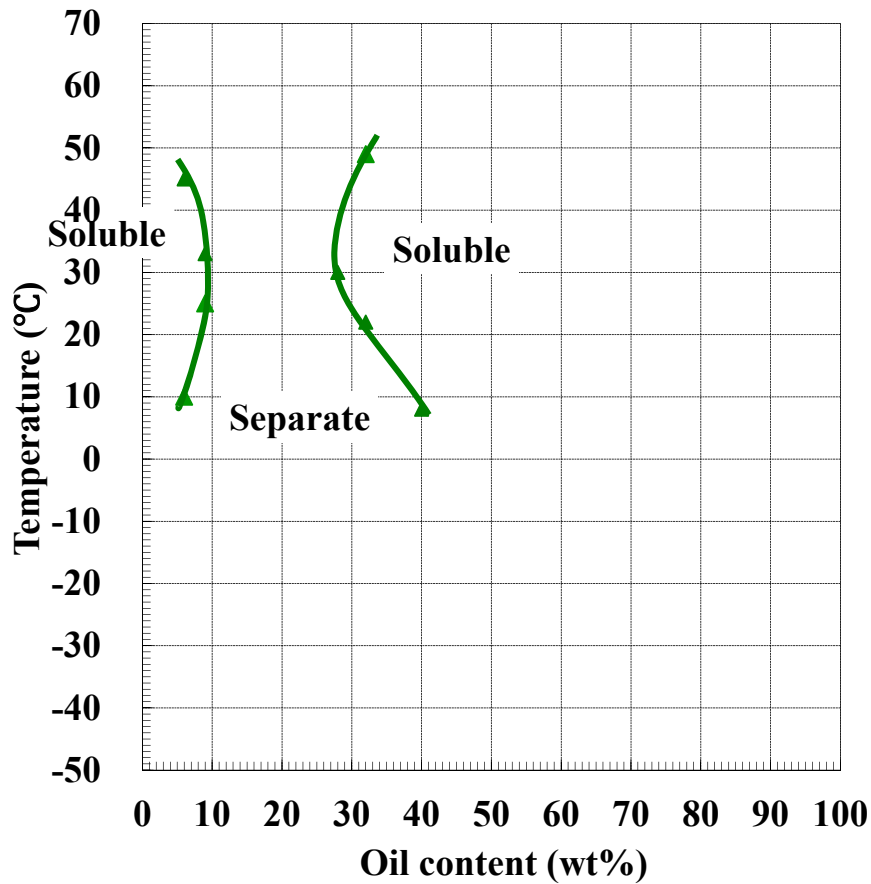
R32



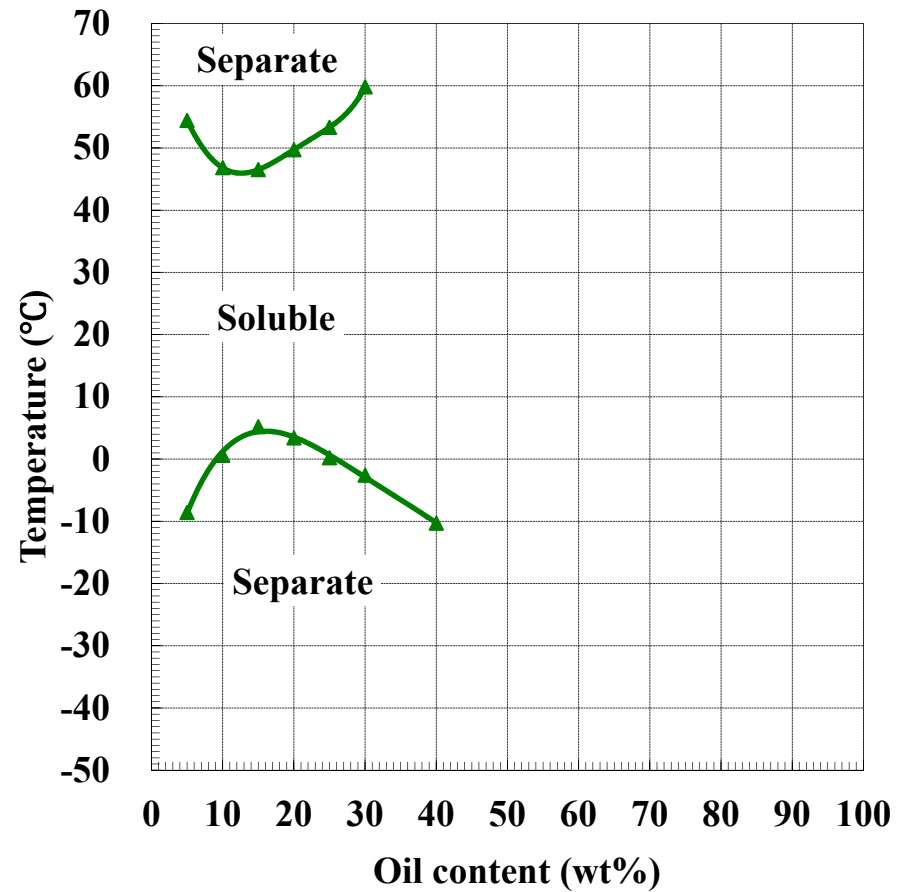
Miscibility of PVE-1A with R32 was lower than that of with R410A.

Miscibility of PVE-2A with R32

PVE-1A



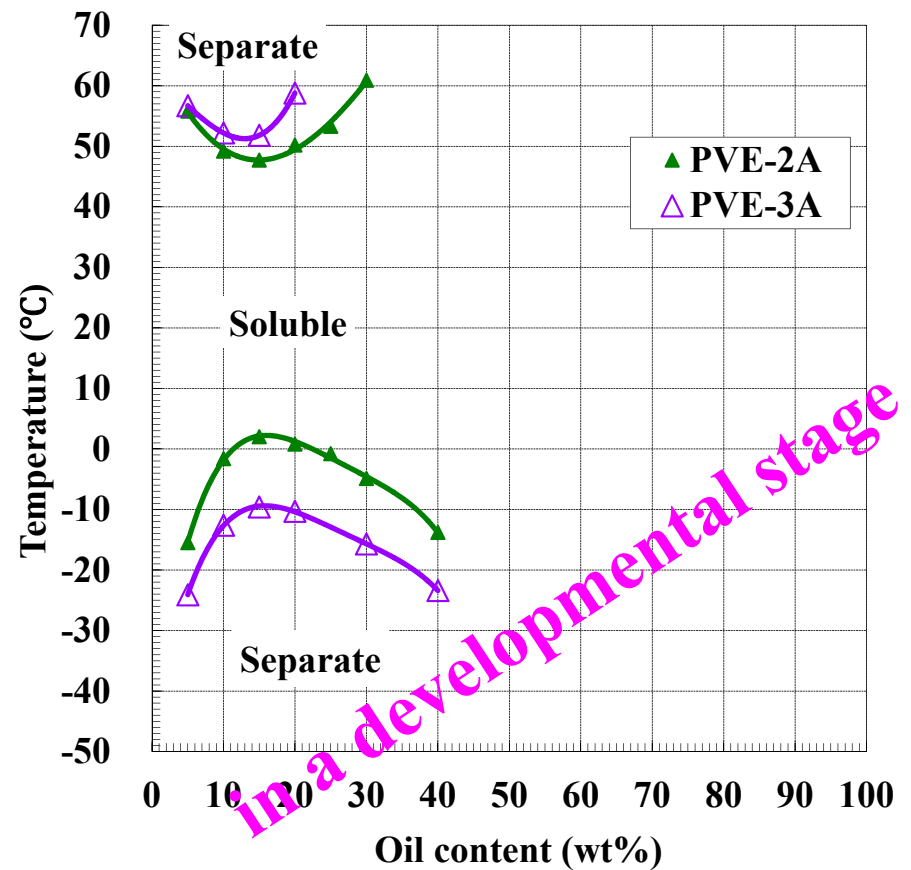
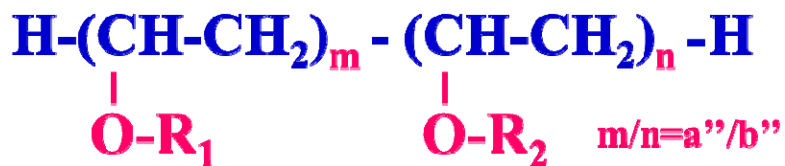
PVE-2A



Miscibility of PVE-2A/R32 was better than that of PVE-1A/R32.

Properties of PVE-3A (special grade for cold area)¹⁰

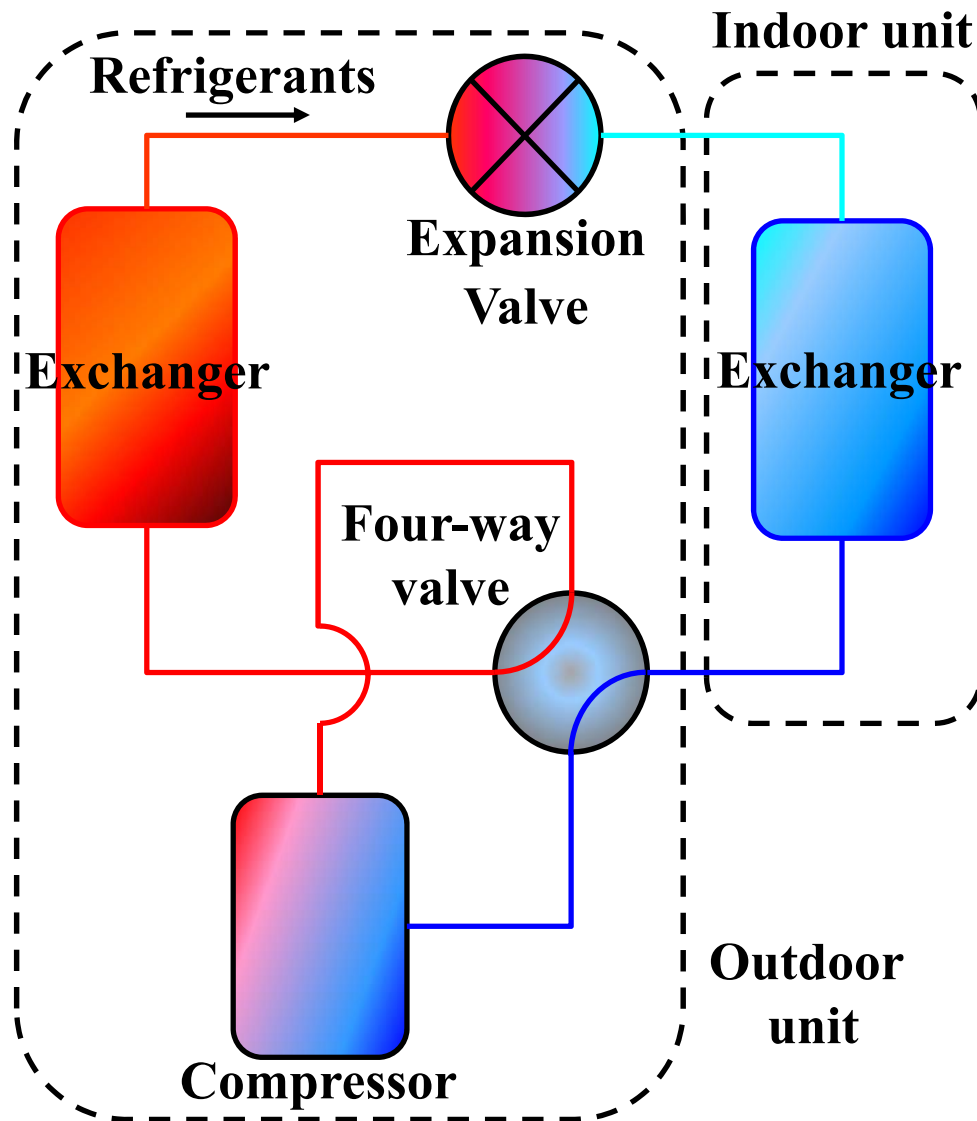
Lubricant	PVE-2A	PVE-3A
Refrigerant	R32	R32
Viscosity @40°C (mm ² /s)	68.41	65.01
Viscosity @100°C (mm ² /s)	8.316	8.030
Viscosity Index	88	88
Density @15°C (g/cm ³)	0.9440	0.9542
Acid Number (mgKOH/g)	0.01>	0.01>
Base Oil	PVE-2	PVE-3



Side chain was adjusted to improved miscibility with R32.

Miscibility of PVE-3A was better than that of PVE-2A.

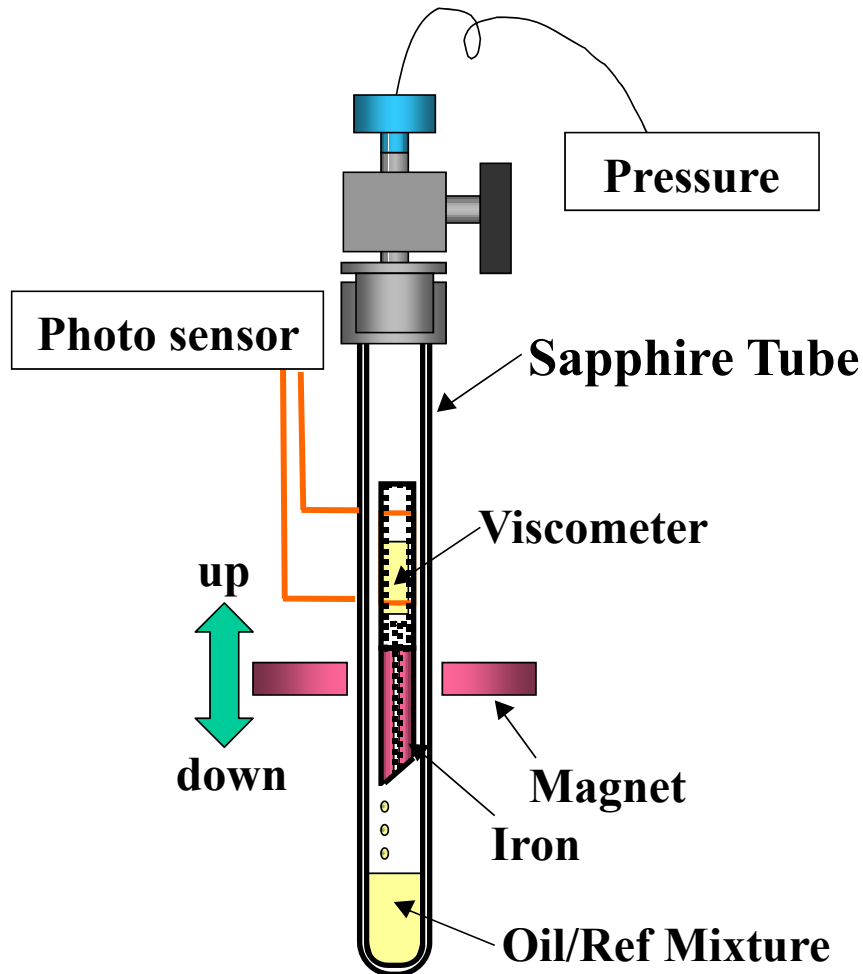
Solubility and Mixture Viscosity of PVEs for R32¹¹



1. Miscibility
2. Solubility
3. Mixture Viscosity
4. Lubricity
5. Volumetric Resistivity
6. Stability
7. Compatibility

Solubility & Mixture Viscosity

12



Detect and Calculation

- Viscosity
 - Pressure
 - Solubility
- } at constant Temp.

Solubility (X_r) is determined as follows :

$$X_r = (W_r - dV_g) / (W_o + W_r - dV_g)$$

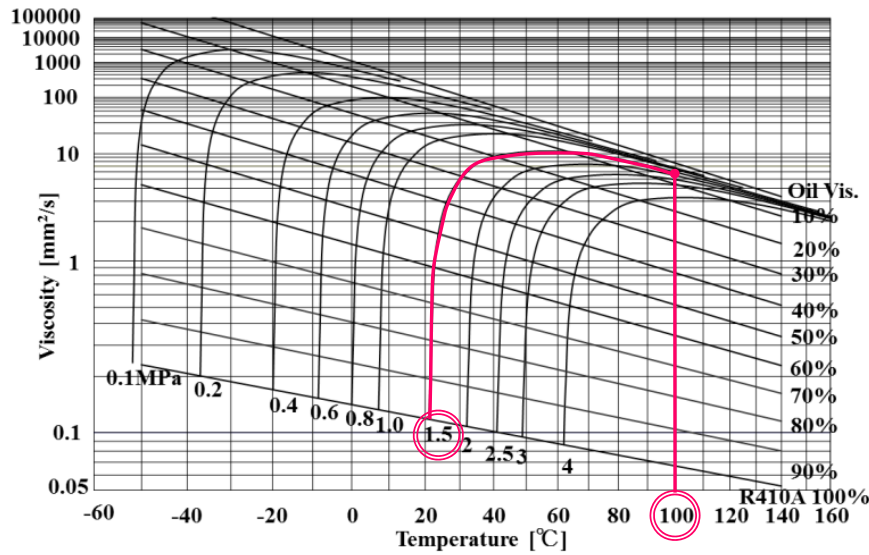
W_o ; the mass of oil

W_r ; the mass of refrigerant

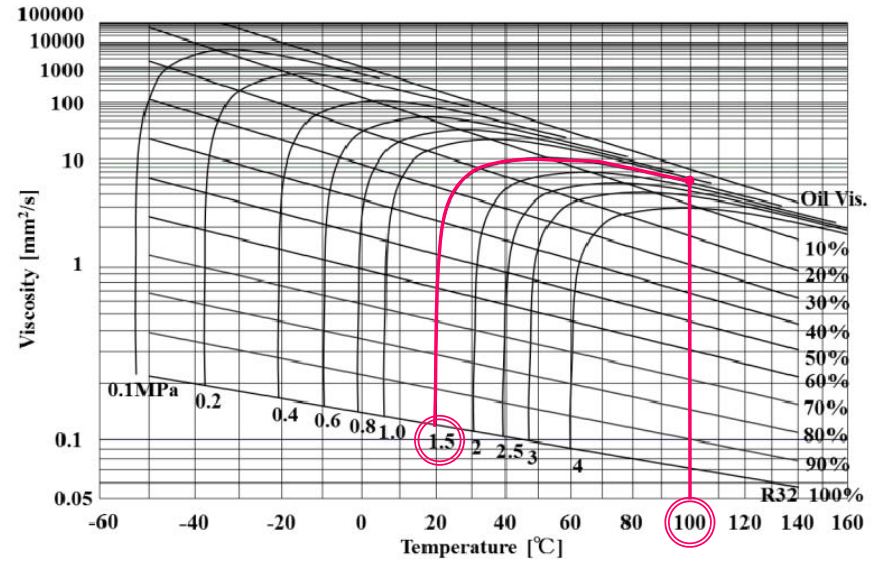
d ; the refrigerant vapor density

V_g ; gas volume at the experimental temperature

Daniel Chart of PVE-2A



PVE-1A/R410A



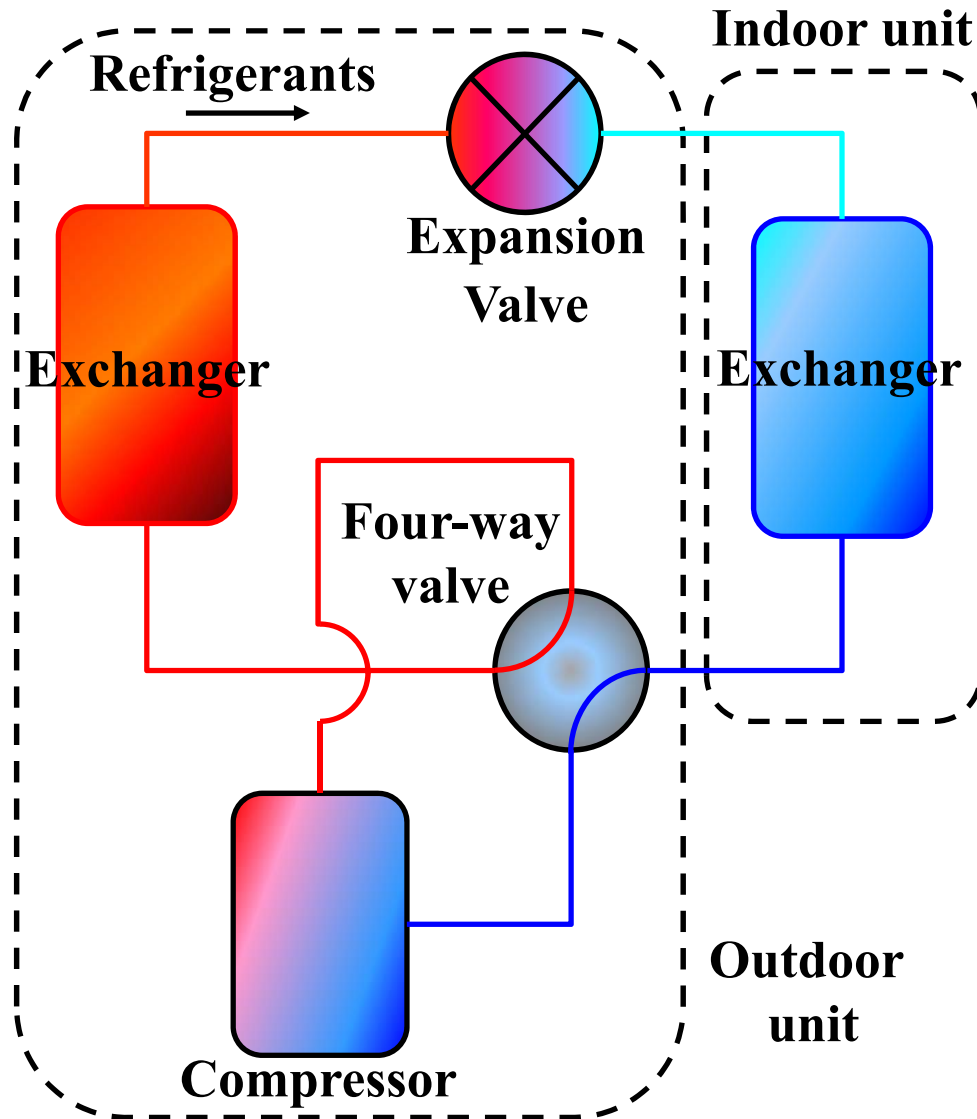
PVE-2A/R32

100°C, 1.5MPa

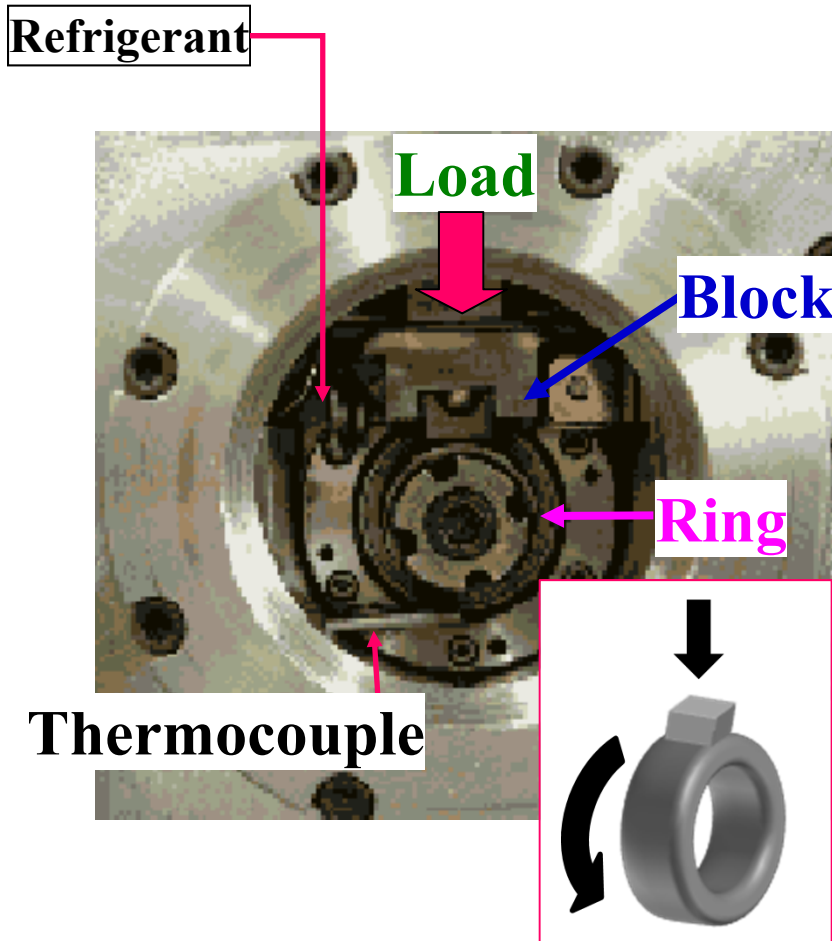
Lubricants	Refrigerants	Solubility (wt%)	Viscosity (mm ² /s)
PVE-1A	R410A	4.6	5.7
PVE-2A	R32	3.5	5.2

Lubricity of PVEs for R32

14



1. Miscibility
2. Solubility
3. Mixture Viscosity
- 4. Lubricity**
5. Volumetric Resistivity
6. Stability
7. Compatibility

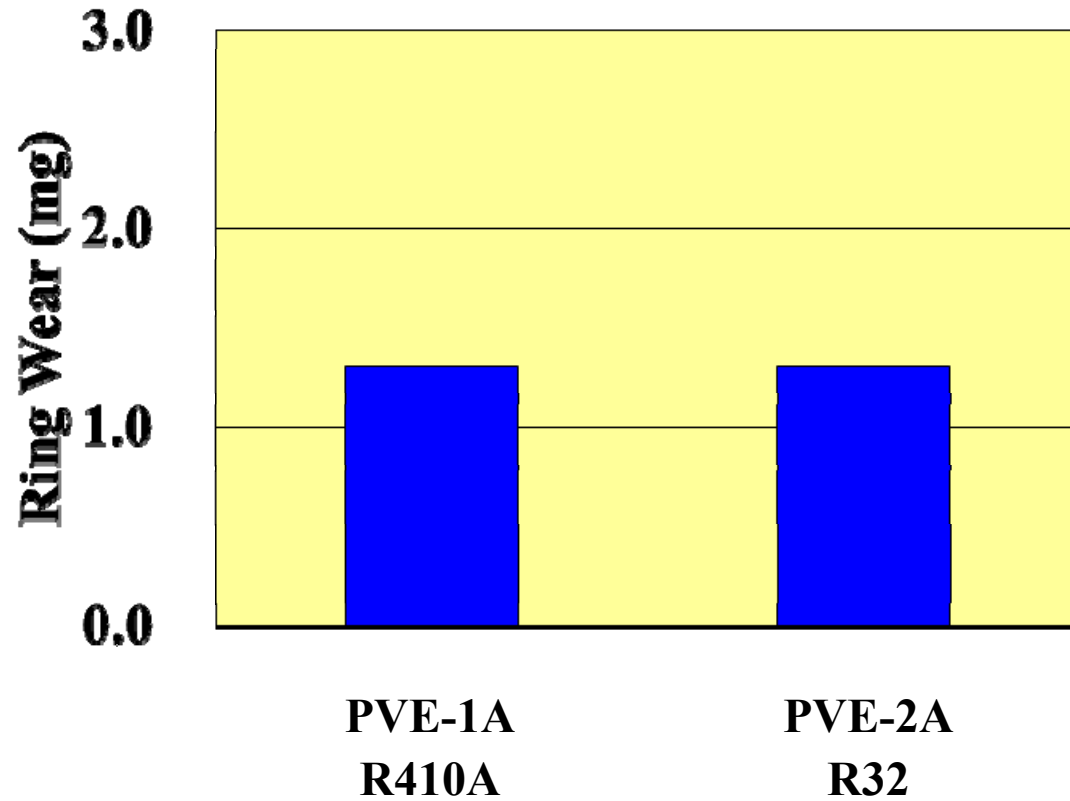


Hermetic Type Block-on-Ring Tester

Lubricity Test Condition

Condition	Test
Temperature (°C)	100
Test Time (min)	60
Oil (g)	250
Refrigerant (MPa)	1.5
Test Piece (Ring)	FC250
Test Piece (Block)	SKH51
Load (N)	1400
Speed (rpm)	1400

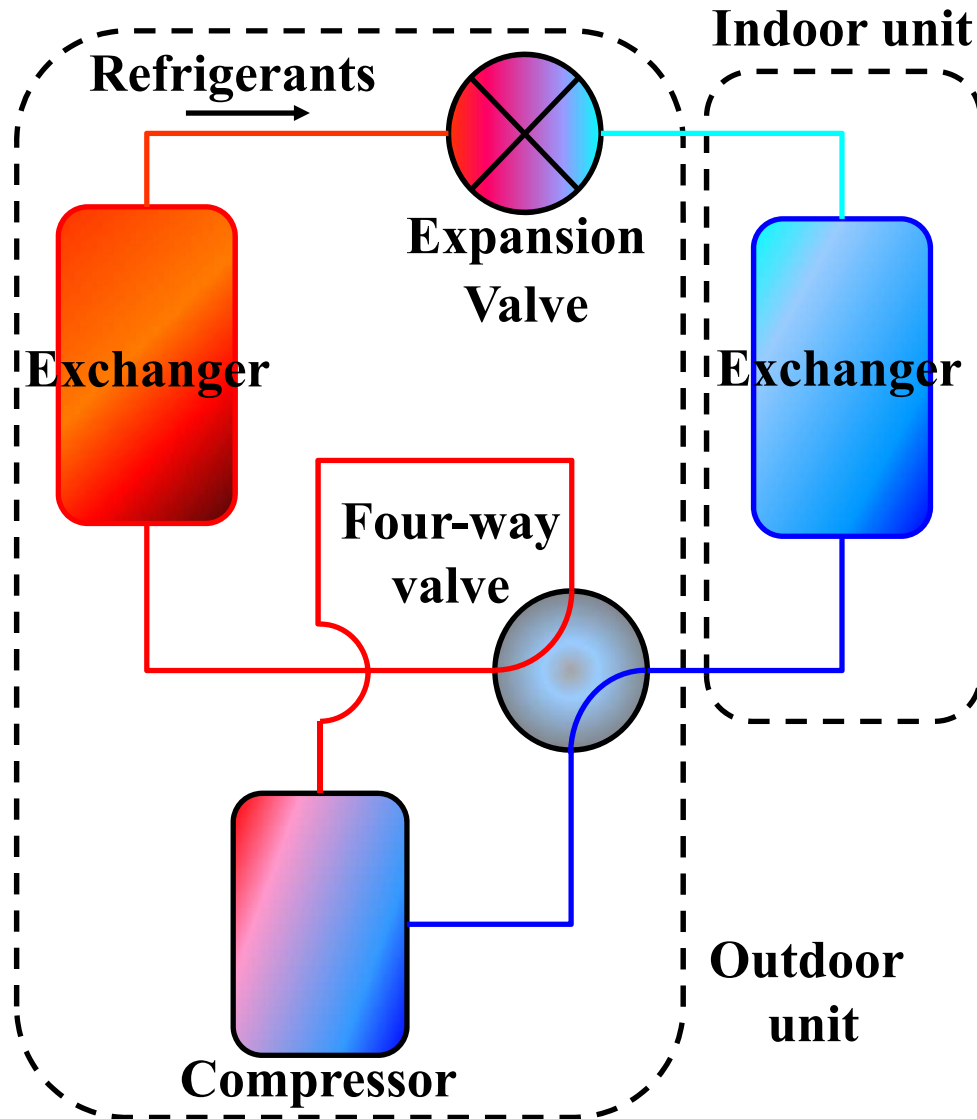
Lubricity of PVE-2A



Lubricities of PVE-2A/R32 and PVE-1A/R410A are same level.

Volumetric Resistivity of PVEs for R32

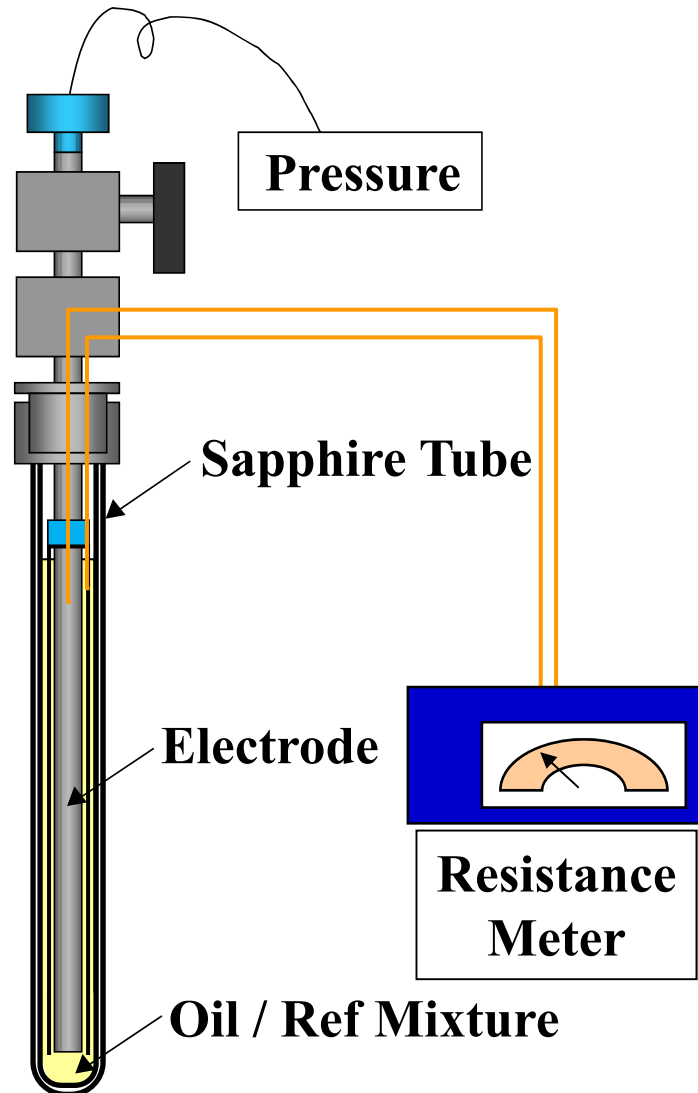
17



1. Miscibility
2. Solubility
3. Mixture Viscosity
4. Lubricity
- 5. Volumetric Resistivity**
6. Stability
7. Compatibility

Volumetric Resistivity

18



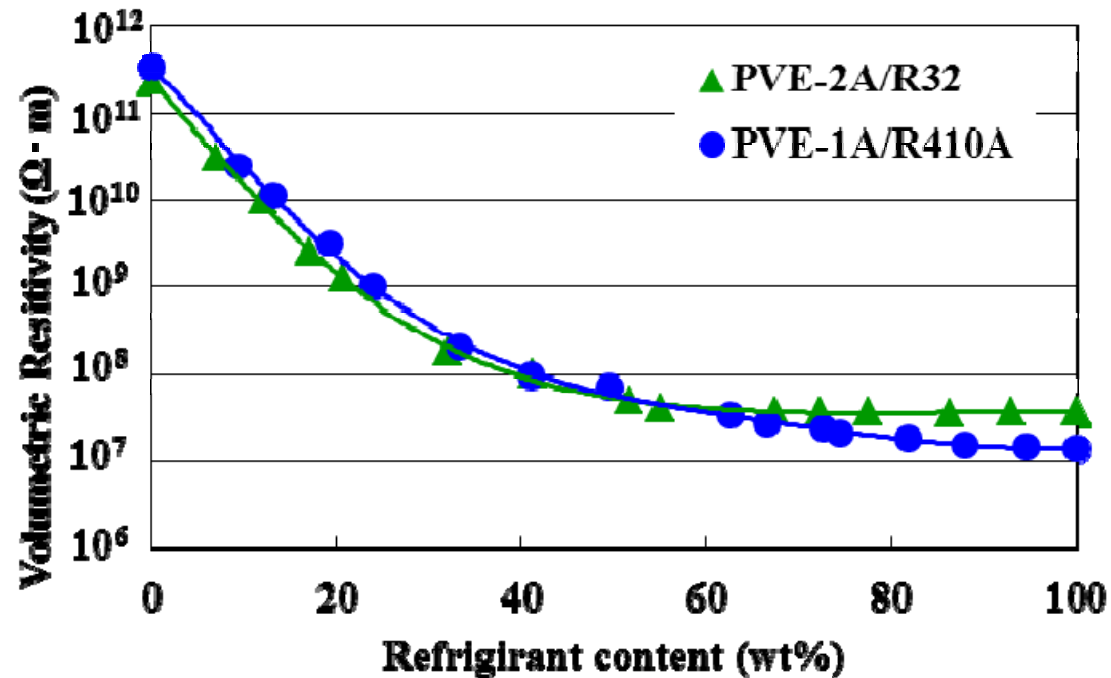
$$\mathbf{I} = \frac{1}{\rho} \mathbf{E}$$

I : Current density (A / m^2)

E : Electrostatic strength (V / m)

ρ : Volumetric Resistivity ($\Omega \cdot \text{m}$)

Volumetric Resistivity of PVE-2A

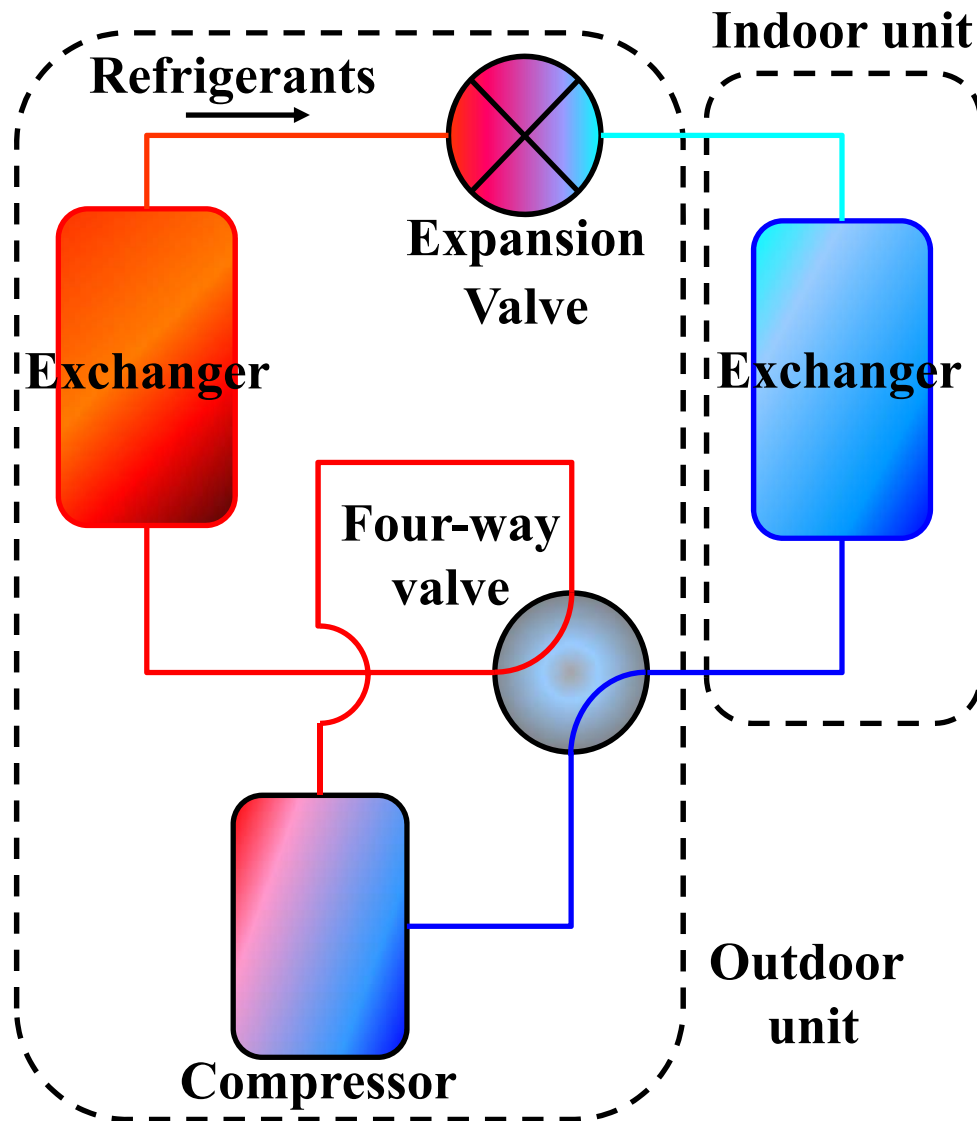


Temperature : 20°C

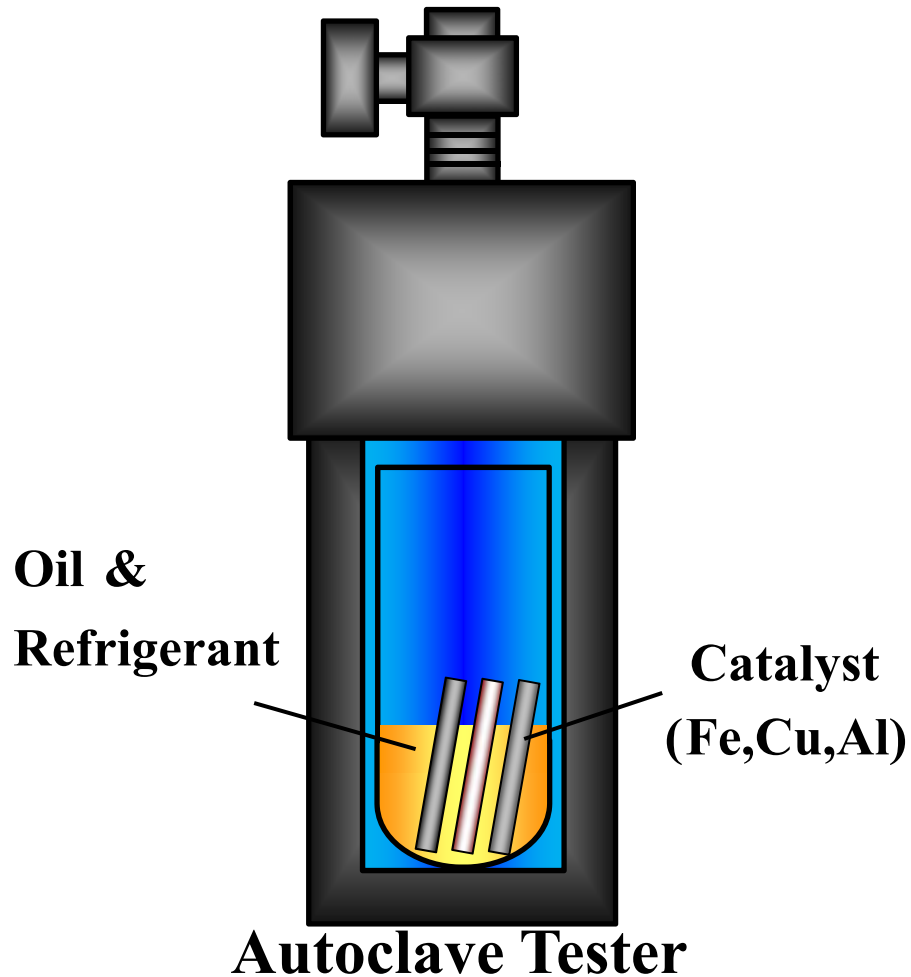
Volumetric Resistivity of PVE-2A/R32 and PVE-1A/R410A were almost same level .

Stability of PVEs for R32

20



1. Miscibility
2. Solubility
3. Mixture Viscosity
4. Lubricity
5. Volumetric Resistivity
- 6. Stability**
7. Compatibility



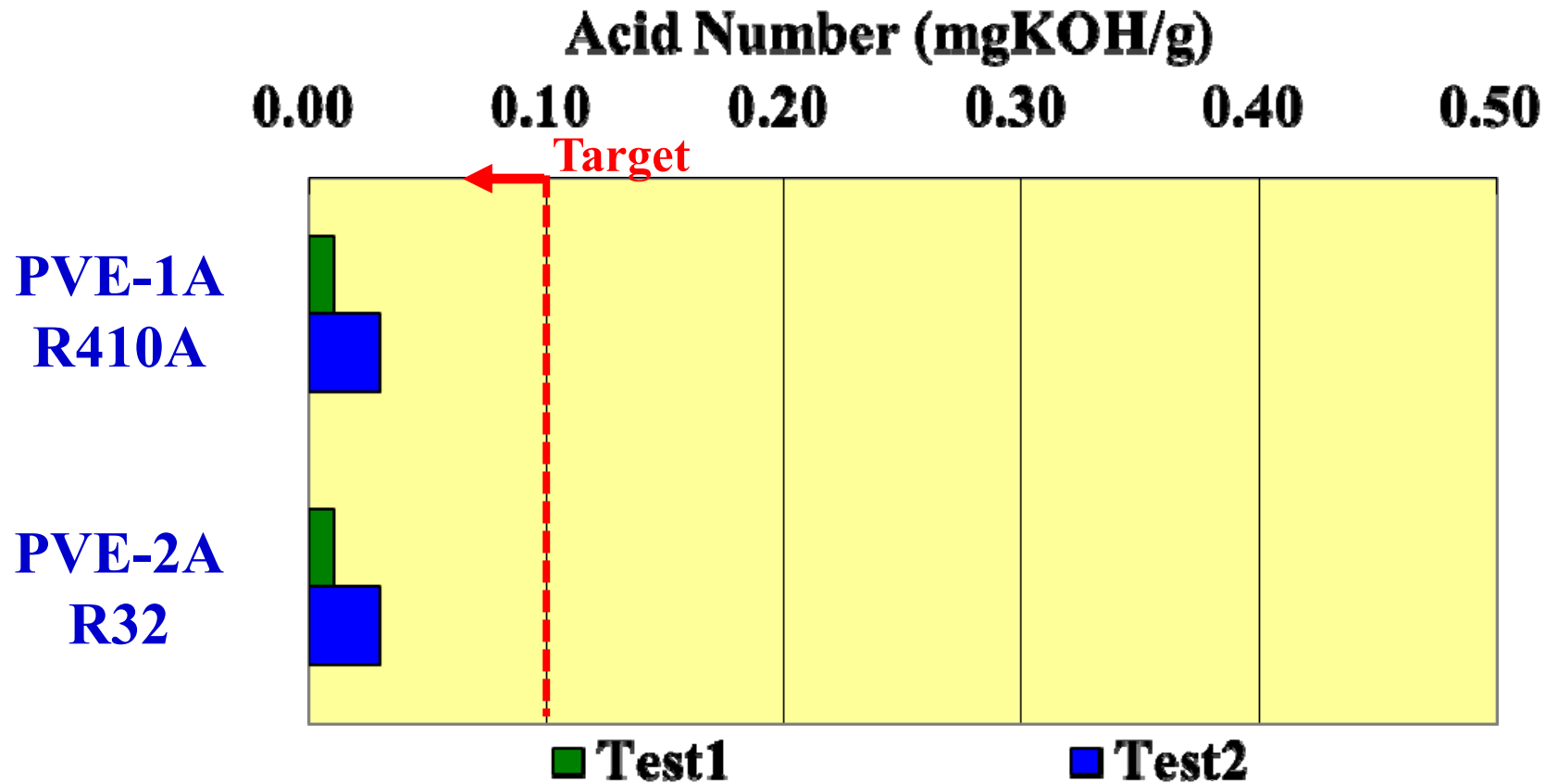
Stability Test Condition

Condition	Test 1	Test 2
Temperature (°C)	175	175
Test Time (day)	14	14
Oil (g)	30	30
Refrigerant (g)	30	30
Water (ppm)	50>	500
Air (Torr)	5>	140
Catalyst	Fe / Cu / Al	Fe / Cu / Al

Condition of Test 1 is for Thermal Stability

Condition of Test 2 is for Hydrolytic & Oxidation Stability

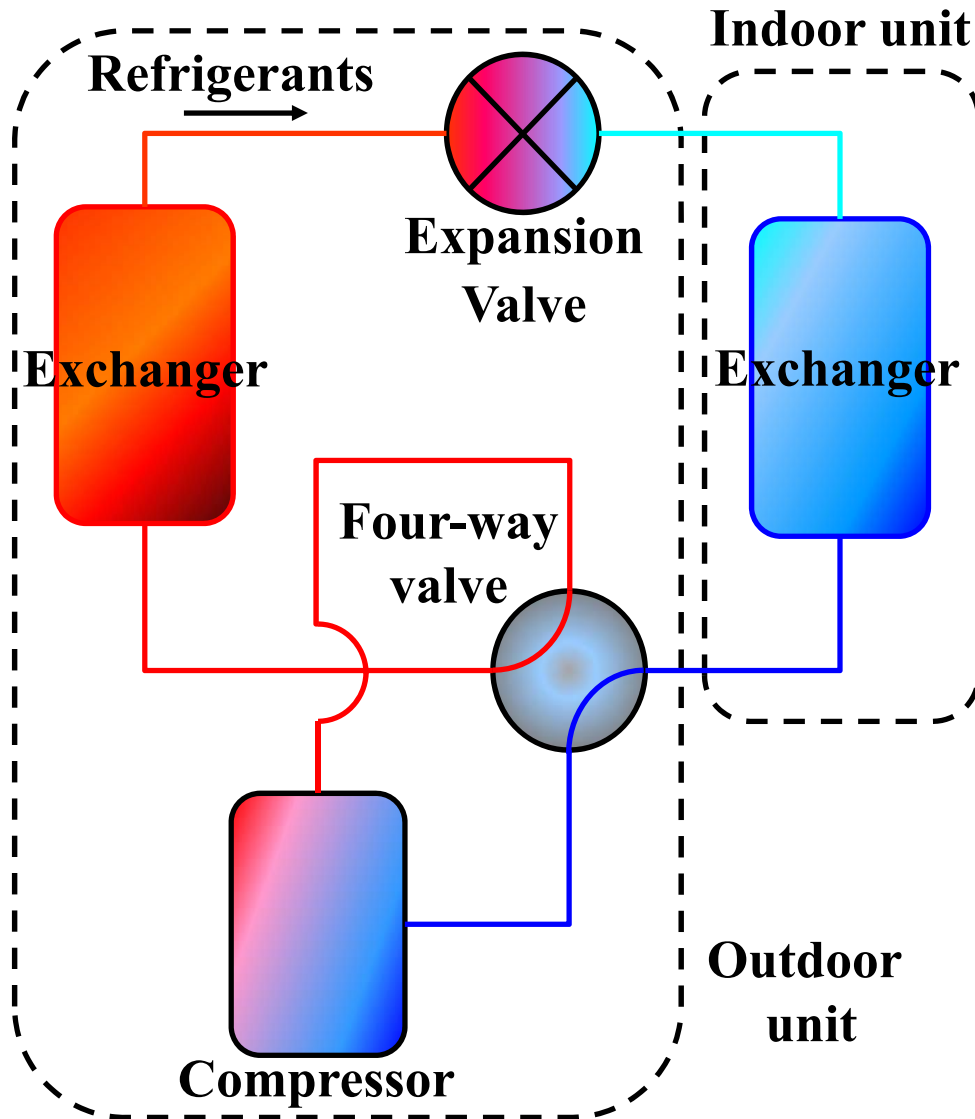
Stability of PVE-2A



Stability is good.

Compatibility of PVEs for R32 with Organic Material

23



1. Miscibility
2. Solubility
3. Mixture Viscosity
4. Lubricity
5. Volumetric Resistivity
6. Stability
- 7. Compatibility**

Compatibility of PVEs for R32 with Organic Material

24

◇ Test Condition of Compatibility

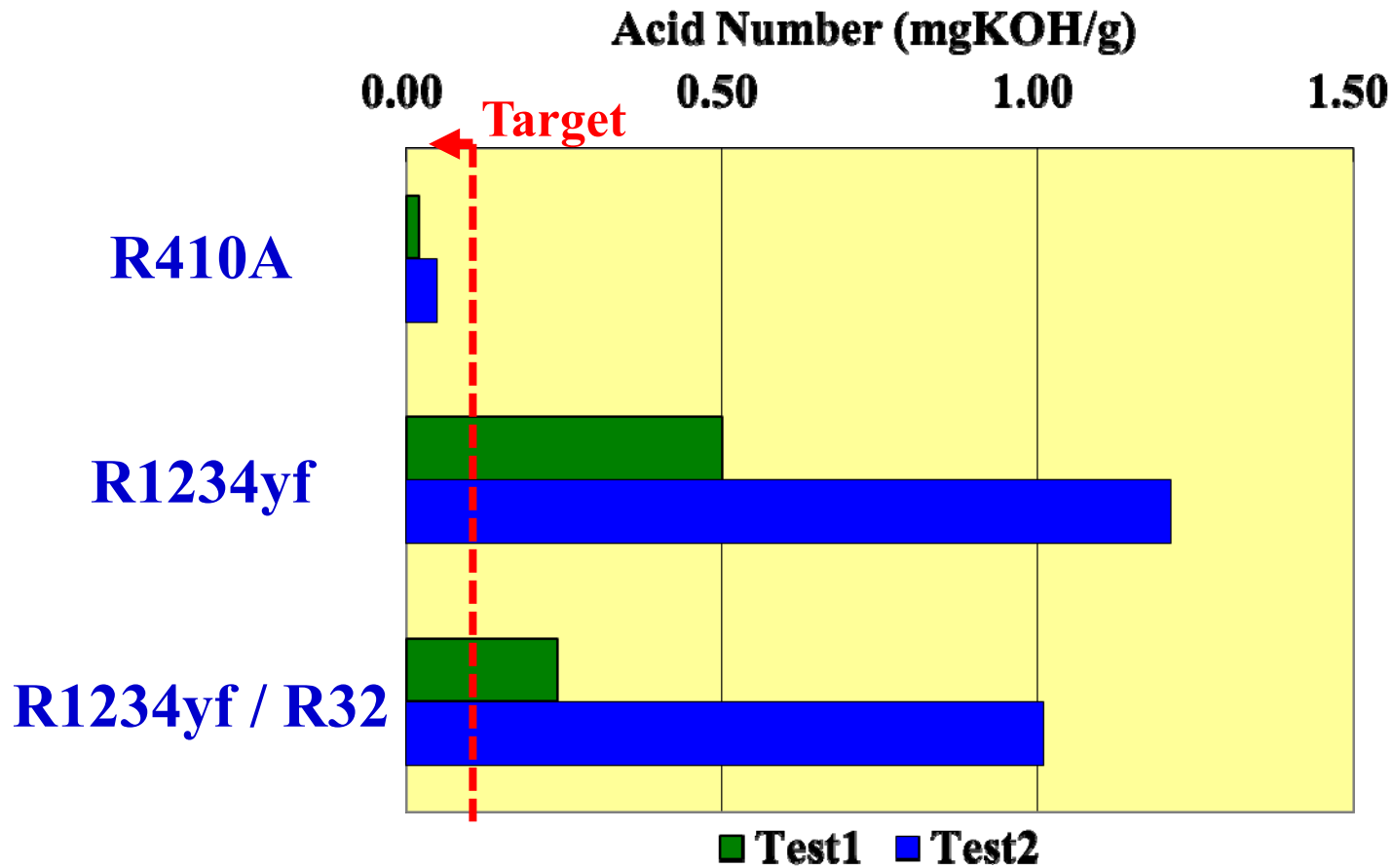
Temp. :140°C, Aging Period:14days, Air: <0.1Torr, Water:<50ppm

Material	Refrigerant	Oil	Acid Number (mgKOH/g)	Appearance of Metal Wire
H-NBR	R410A	PVE-1A	0.01	no change
	R32	PVE-2A	0.01	no change
PET	R410A	PVE-1A	0.02	no change
	R32	PVE-2A	0.02	no change
PBT	R410A	PVE-1A	0.03	no change
	R32	PVE-2A	0.03	no change
PEN	R410A	PVE-1A	0.02	no change
	R32	PVE-2A	0.02	no change
PTFE	R410A	PVE-1A	0.01	no change
	R32	PVE-2A	0.01	no change
PPS	R410A	PVE-1A	0.00	no change
	R32	PVE-2A	0.00	no change

for HFO(R1234yf)

Stability of PVE-1A

26



**R1234yf and R1234yf / R32 showed higher acid number.
⇒ Stability of R1234yf was less than that of R410A.**

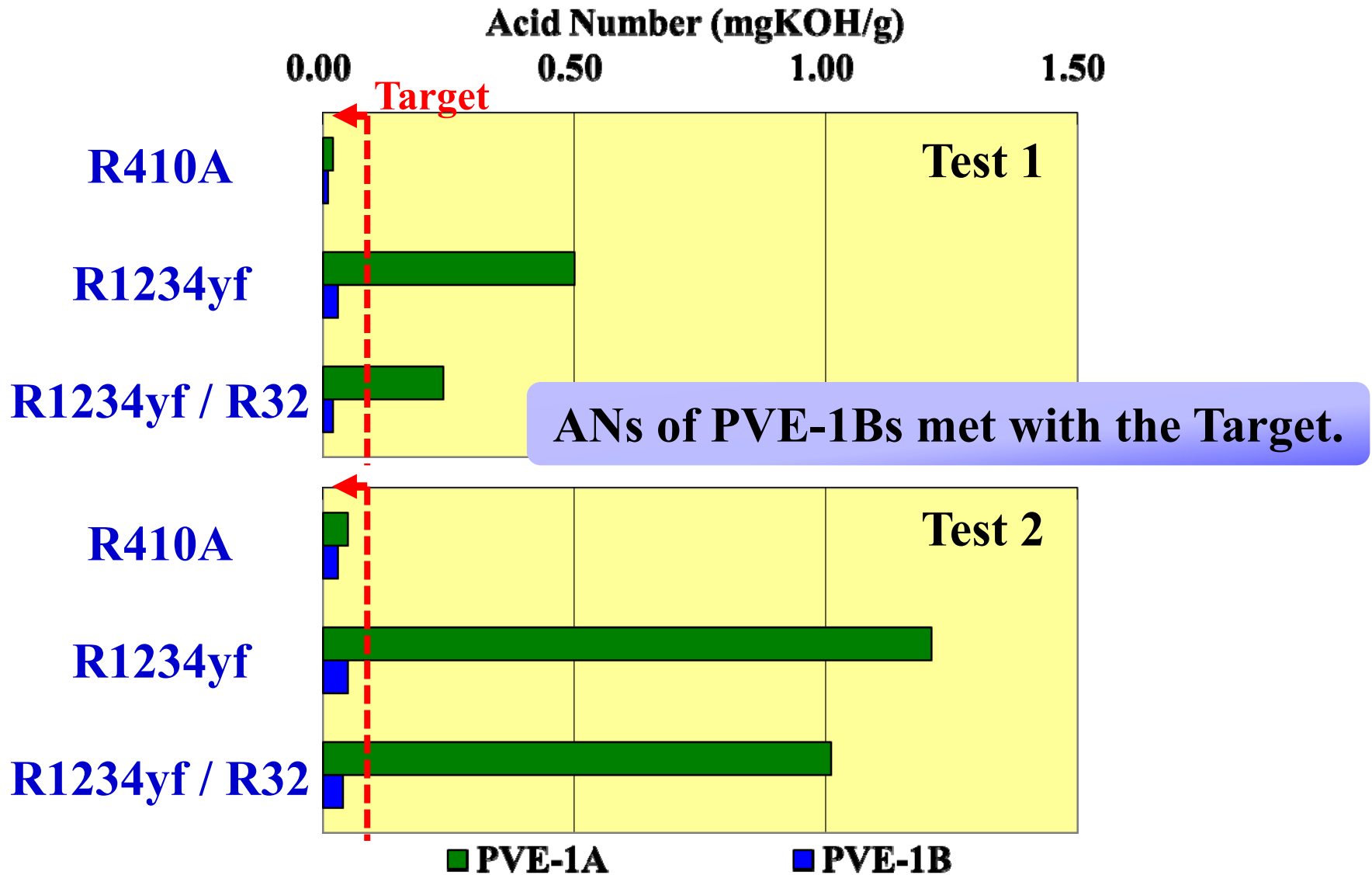
Specification of PVE-1B

Lubricant	PVE-1A	PVE-1B
Refrigerant	R410A	R1234yf
Viscosity @40°C (mm ² /s)	66.57	66.86
Viscosity @100°C (mm ² /s)	8.037	8.073
Viscosity Index	84	84
Density @15°C (g/cm ³)	0.9369	0.9370
Acid Number (mgKOH/g)	0.01>	0.01>
PVE type	PVE1	PVE1
additive	antiwear	include
	antioxidant	include
	acid catcher	include
	New compound	-

⇒ B

PVE-1B was included additive of the New compound.

Stability of PVE-1B



For R32

- **New PVE(PVE-2A) was improved miscibility with R32 compared to current PVE(PVE-1A) by adjusting chemical structure.**
- **New PVE/R32 showed equal lubricity, volumetric resistivity, stability and compatibility compared to current PVE/R410A.**

For HFO(R1234yf)

- **New Formulation(PVE-1B) showed better stability with R1234yf compared to current PVE(PVE-1A).**

Thank you!