The Development of Capped-PAG Refrigeration Lubricants for Automotive A/C with CO_2 and HFC152a

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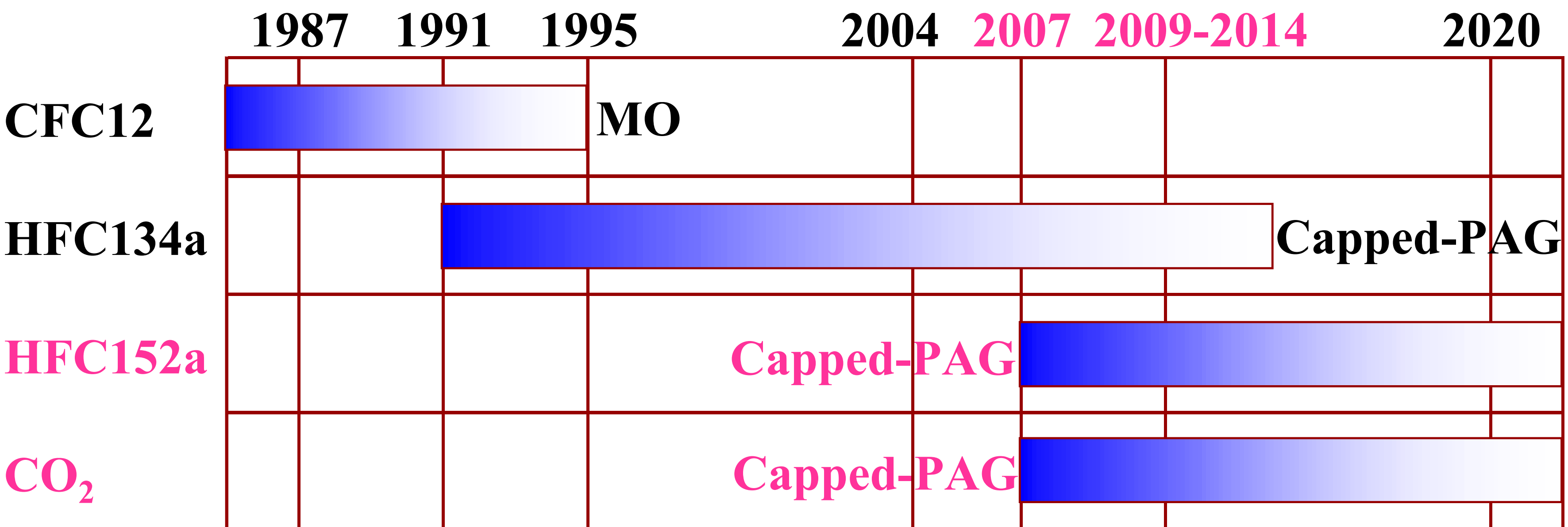
The Trend of the Refrigerating Oils for CO_2 and HFC152a



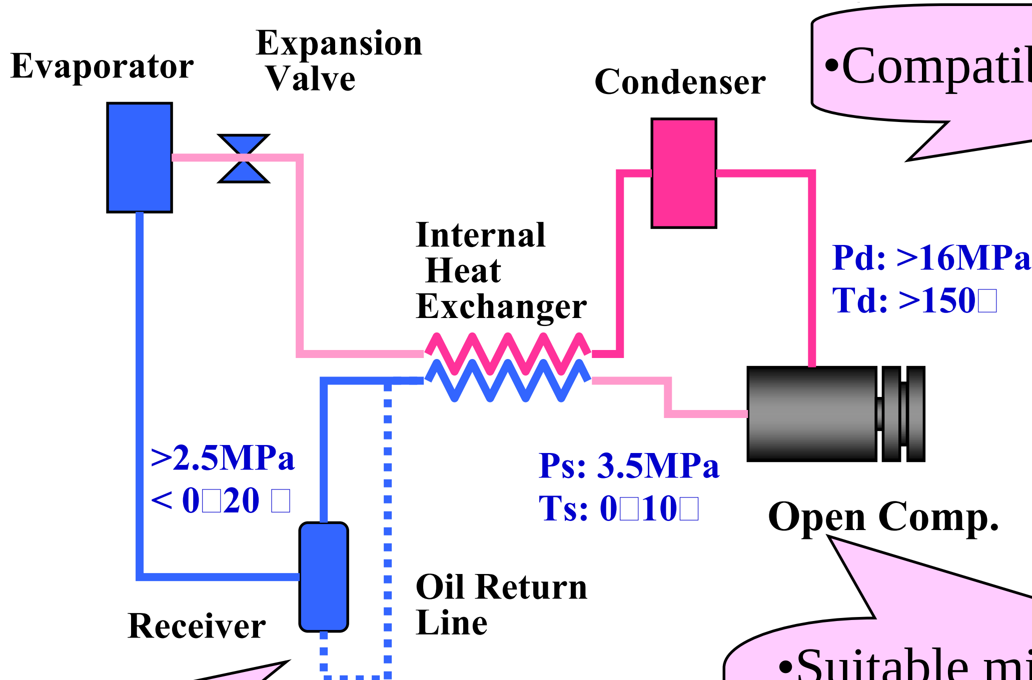
1987□ Direction of Inhibition for CFC and HCFC (The Montreal Protocol)

1997□ Protective Action for the Global Warming (The Kyoto Protocol)

2009(?) □ EU regulation

2020□ End of HCFCs

Refrigerating Oil Requirement with CO_2 Automotive A/C System



- Compatibility with various material

- Suitable mixture viscosity
- Lubricity under extreme-pressure
- Stability under supercritical condition
- Stability under high temperature

- Miscibility with CO_2

□ ***Capped-PAG is the best lubricant!***

Chemical Structure of Capped-PAG

$$\mathrm{CH_3\text{-}O\text{-}(\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3}$$

□Main Chain : Good Stability and No Hydrolysis

□End Cap : Good Lubricity and Solubility

□Free Design of m/n □ Flexibility to alter Miscibility

□Free Design of m+n □ Flexibility to alter Viscosity □

□

Comparison with PAGs and POE of Bonding Energy and pKa

Bonding Type		C-H	C-C	C-O	C=O	O-H
Bonding Energy	σ -Bonding	98.9	83.1	84	84	103
	π -Bonding	□	□	□	66	□
	resonance	□	□	□	24	□
	(Total)	□	□	□	-174	□
pKa		□	□	□	□	15.8
Bonding length(□)		1.09	1.54	1.48	1.23	□
Capped-PAG					□	□
Normal-PAG					□	
POE						□
Chemical Stability		good			bad	

$CH_3\text{-}O\text{-}(CH(CH_3)\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$

Capped-PAG

$HO\text{-}(CH(CH_3)\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}Bu$

normal-PAG

$C\text{-}(CH_2\text{-}O\text{-}C(=O)\text{-}R)_4$

POE

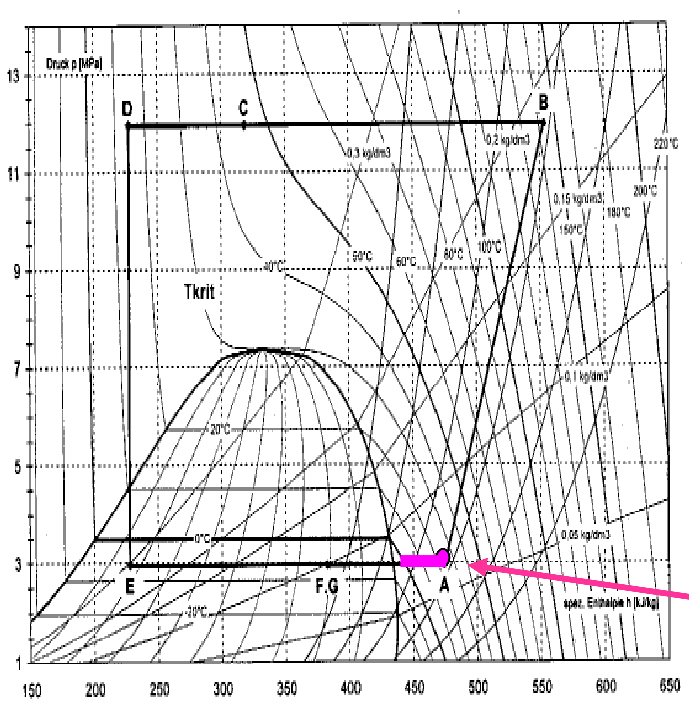
POE□π-Bonding → Hydrolysis , Tribochemical Reaction

Normal-PAG : pKa → Decrease of the Fatigue Life

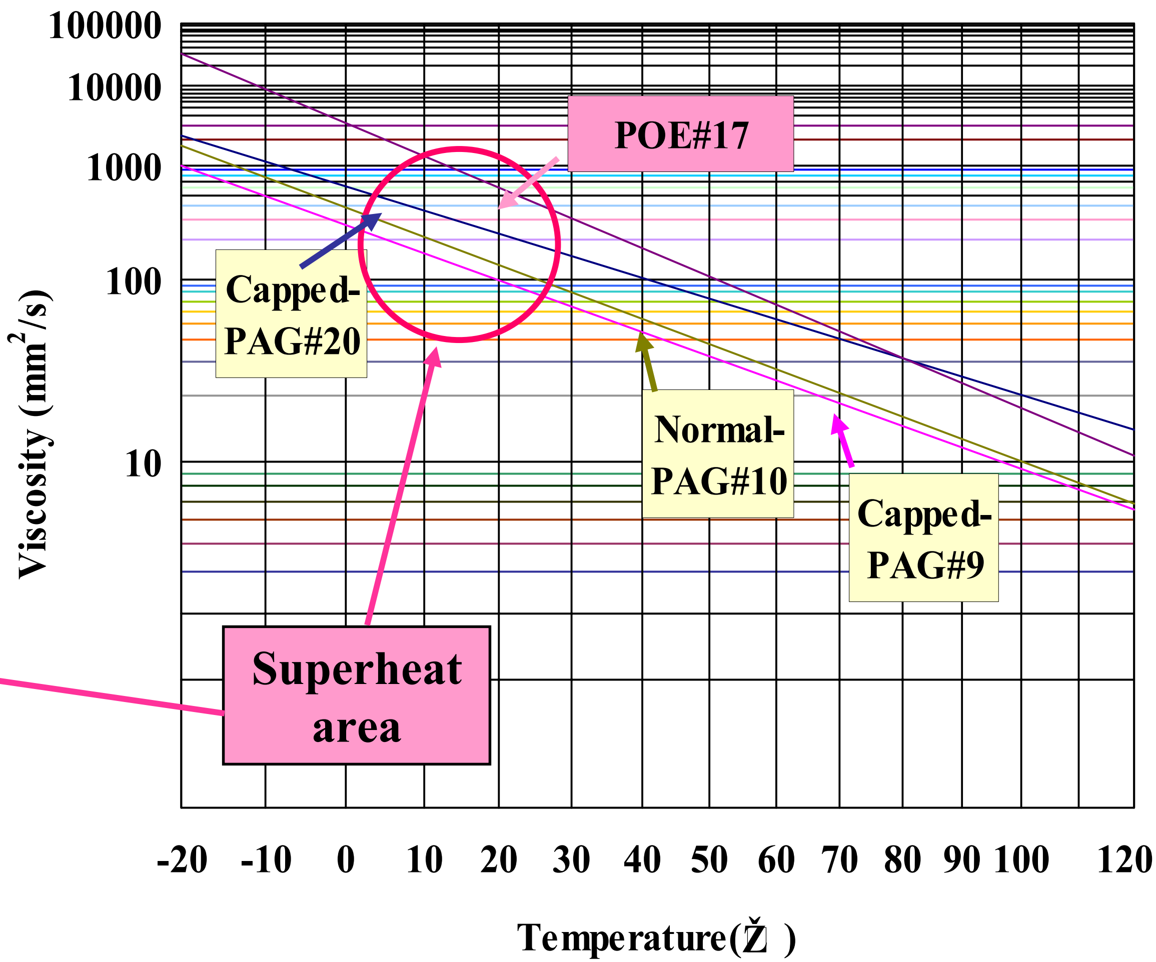
General Specification of PAGs and POE

	Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#17
Viscosity(@ -20□)mm^2/s	1033	2166	1697	30900
Viscosity(@ 40□) mm^2/s	43.32	100.1	51.62	168.6
Viscosity(@100□)mm^2/s	9.234	20.01	9.816	17.13
Viscosity Index	203	225	179	109
Density(@15□) g/cm^3	0.9944	1.0195	0.9973	0.9719
Pour Point □	-45	-45	-45	-32.5
Acid Number mgKOH/g	0.01	0.05	0.01	0.02

Property of Oil return at Superheat of PAGs and POE with CO_2 □

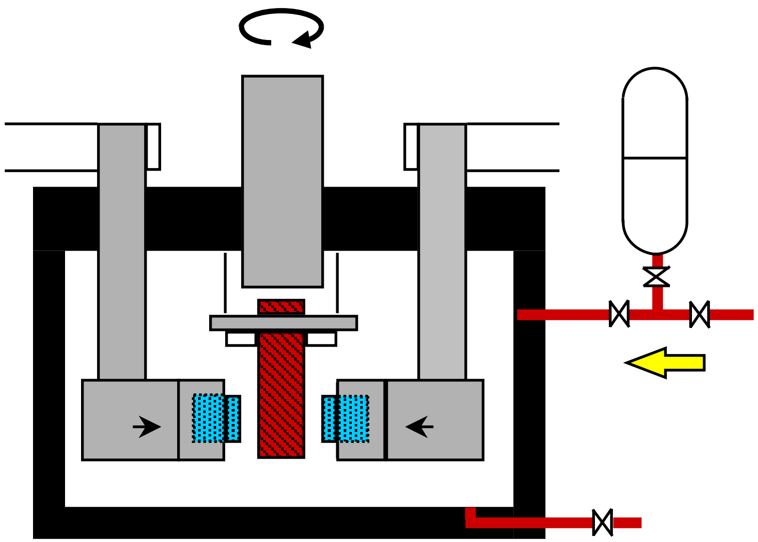


CO_2 P-h Diagram



Viscocity-Temperature Chart

Lubricity of PAGs and POE
(Test Apparatus and Condition)



: Pin

: V Block

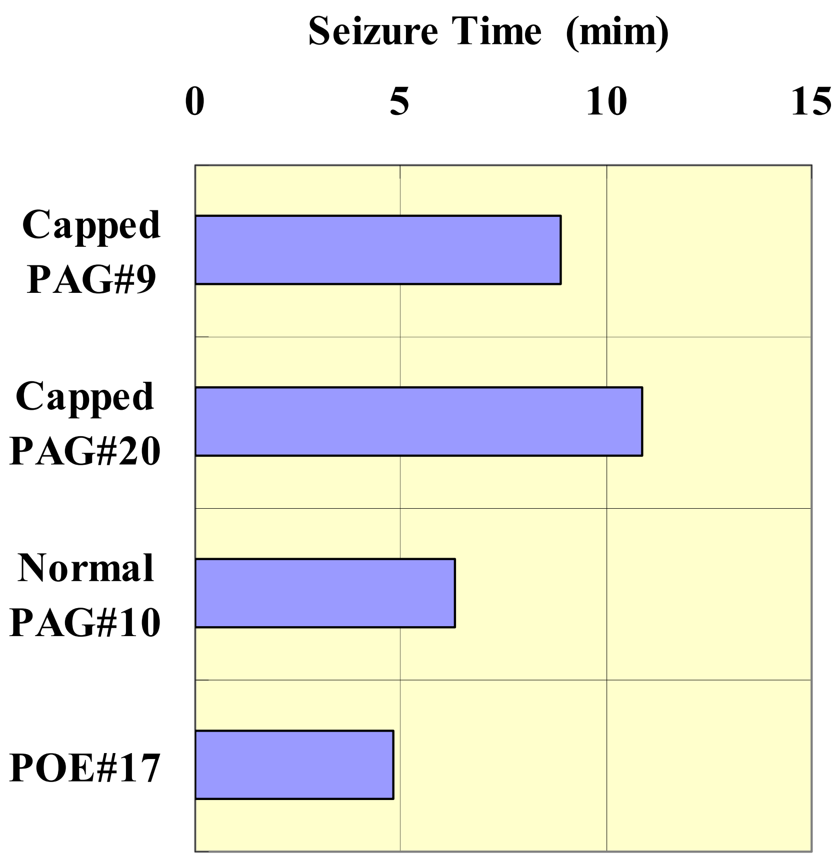
Refrigerant/Oil

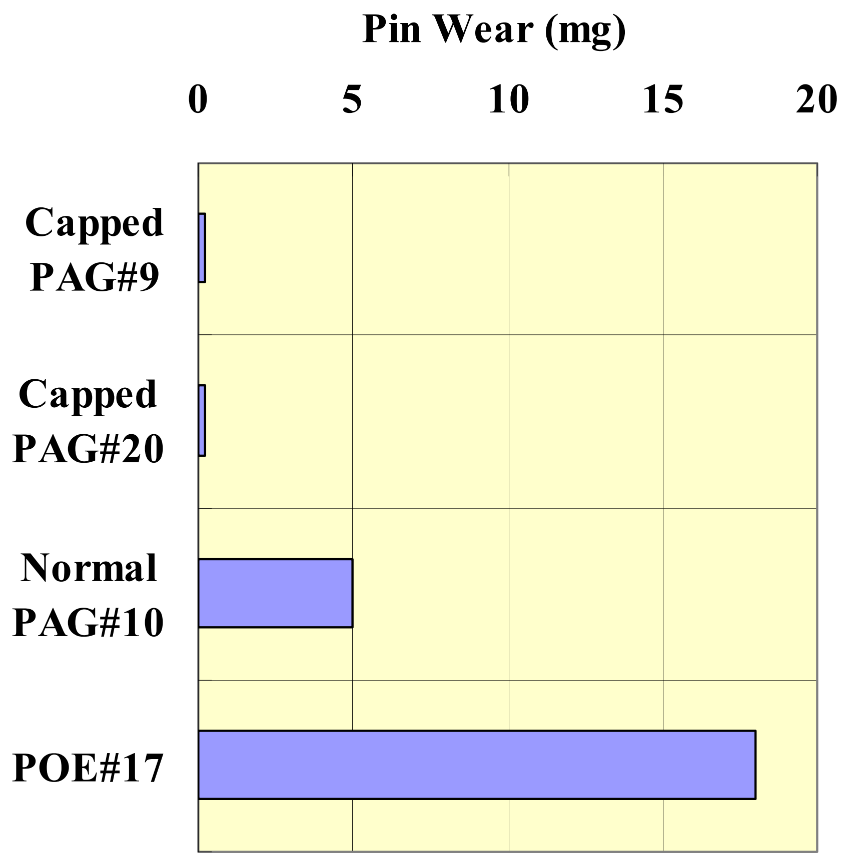
Hermetic Type Falex Tester

Test Condition

	Seizure	Wear
Pin	SUJ2	SCM415
Block	SUJ2	SUJ2
Speed (m/s)	0.15	0.1
Load (N)	667	1780
Time (min)	□	60
Temperature(□)	RT	50
Oil	4μl	200(cc)
Pressure of CO_2 □MPa)	1	1

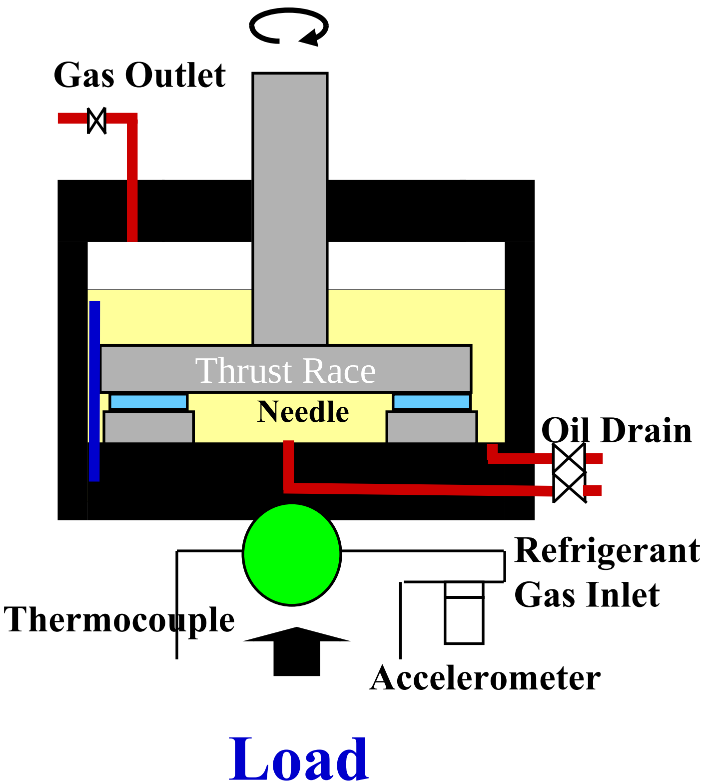
Seizure Time and Wear





Fatigue Life of PAGs and POE

(Test Apparatus and Condition)

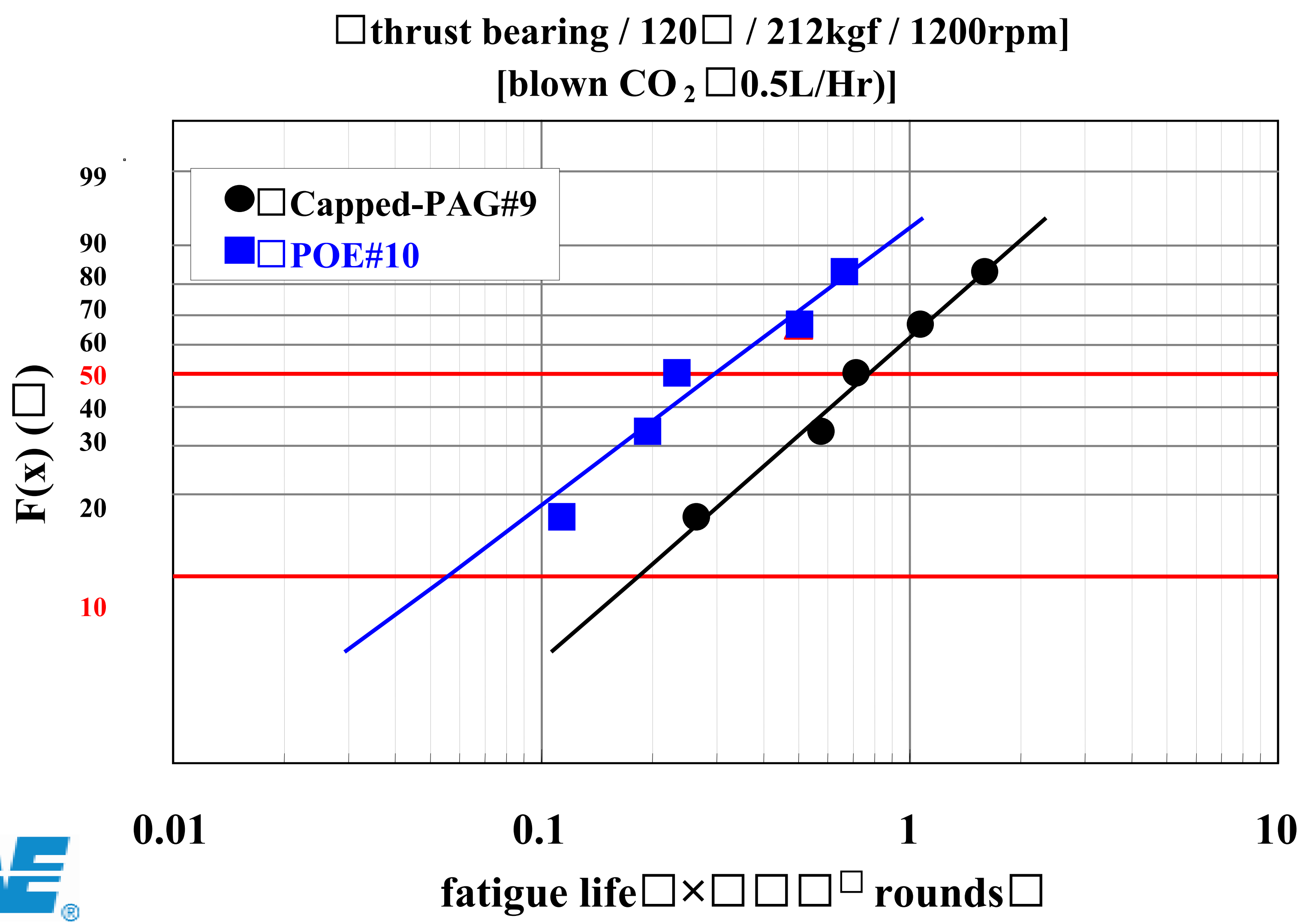


Fatigue Life Tester

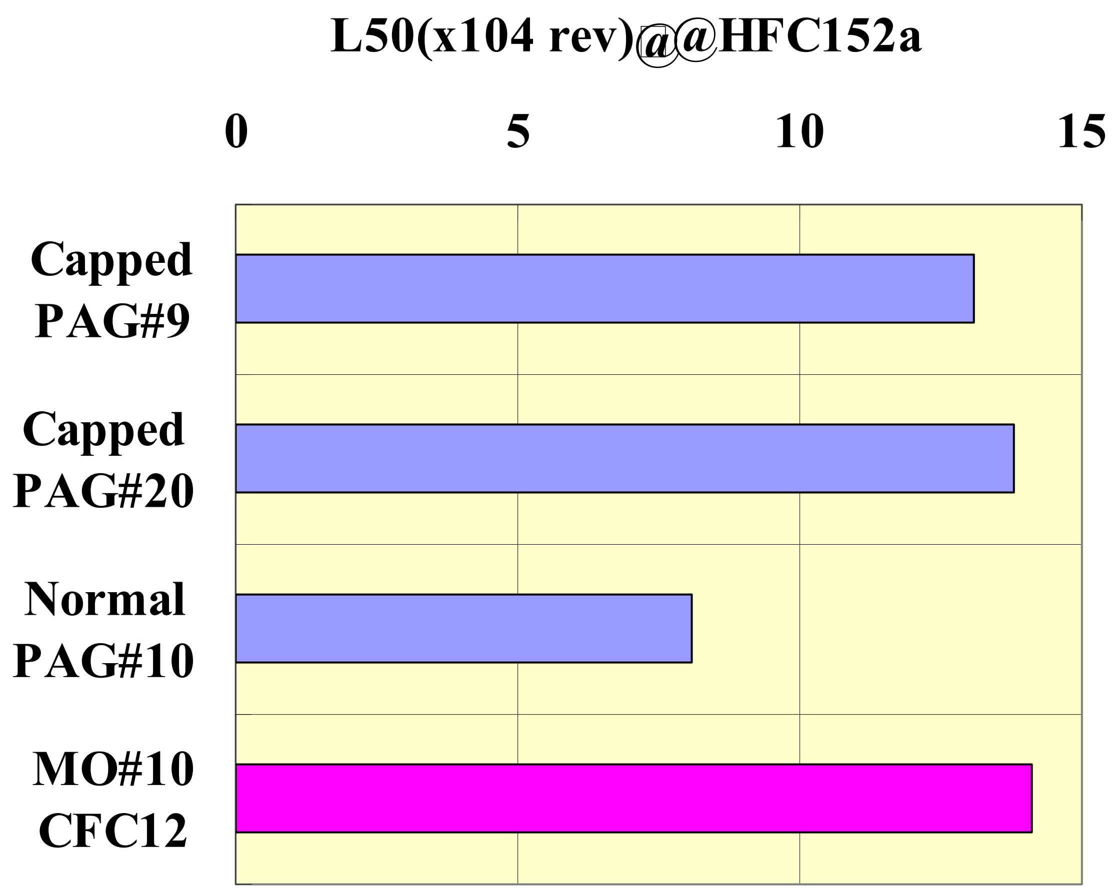
Test Condition

		SUJ2	SUJ2
Needle or Ball		**SUJ2 φ 18x5.55mm (3 needles)**	**SUJ2 φ 9.5mm (3 balls)**
Disc		**SUJ2 Plate**	**SUJ2 Plate**
Pmax	**(GPa)**	**2.23**	**5.9**
Frequency of Contact	**(Rev./min.)**	**1200**	**2700**
Temperature	**(□)**	**120**	**80**
Oil	**（cc）**	**150**	**150**
Refrigerant	**□L/hr)**	**0.5(CO_2)**	**0.5(HFC152a)**

Fatigue Life of Capped-PAG and POE with CO_2



Fatigue Life of Capped-PAG and Normal-PAG

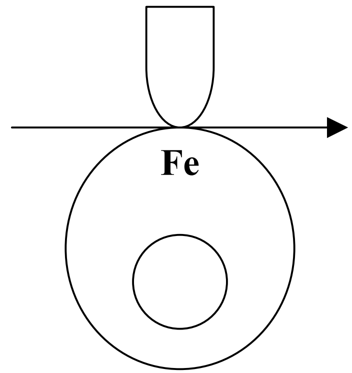


Tribochemistry of PAGs

CH_3 (branch)

$CH_3\text{-}O\text{-}(CH(CH_3)\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$

Capped-PAG



CH_3 (branch)

$CH_3\text{-}O\text{-}(CH(CH_3)\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$

No Reaction

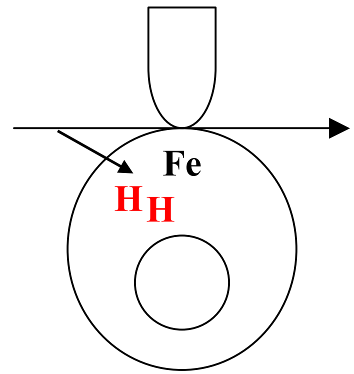
⬇

Good Lubricity

CH_3 (branch)

$HO\text{-}(CH(CH_3)\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}\ Bu$

Normal-PAG



CH_3 (branch)

$O\ =(C(CH_3)\text{-}\ CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}\ Bu$

Hydrogen Brittleness

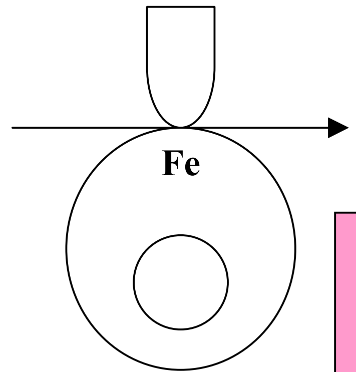
⬇

Decrease Fatigue Life

Tribochemistry of POE

O
||
$C-(CH_2-O-C-R)_4$

POE



O
||
Fe^{+} -O-C-R

O
||
Fe^{2+} $(-O-C-R)_2$

Iron Carbonate Soap

⬇

Seizure,Wear,Fatigue Life

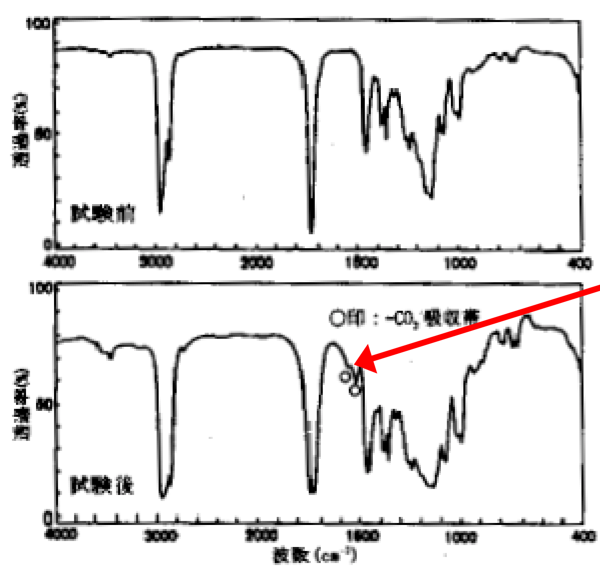


図4. HS-POEのIRチャート

1520□1560 cm^{-1}

Carbonium ion($-CO^{2-}$□

C-O Bond Stretching Vibration

Stability of PAGs and POE

□Factor□	□EFFECT□
Heat	Thermal Decomposition
Oxygen in Air	Oxidation
Water	Hydrolysis

Thermal ,Oxidative and Hydrolytic Stability

Stability Tests Method

CO_2 Autoclave Test

	Thermal Stability Test	Oxidative Stability Test	Hydrolytic Stability Test
Temperature(□)	200		
Time (days)	10		
Oil (g)	50		
CO_2 (g)	10		
Air (cc)	□	50	□
H_2O (ppm)	□	□	300
Cat.	Fe,Cu,Al		

HFC152a Sealed Tube Test

	Thermal Stability Test	Oxidative Stability Test	Hydrolytic Stability Test
Temperature(□)	175		
Time (days)	10		
Oil (g)	4		
HFC152a (g)	1		
Air (torr)	□	50	□
H_2O (ppm)	□	□	2000
Cat.	Fe,Cu,Al		

Stability of PAGs and POE with CO_2

(CO_2 Autoclave Test Results)

CO2 Thermal Stability Test

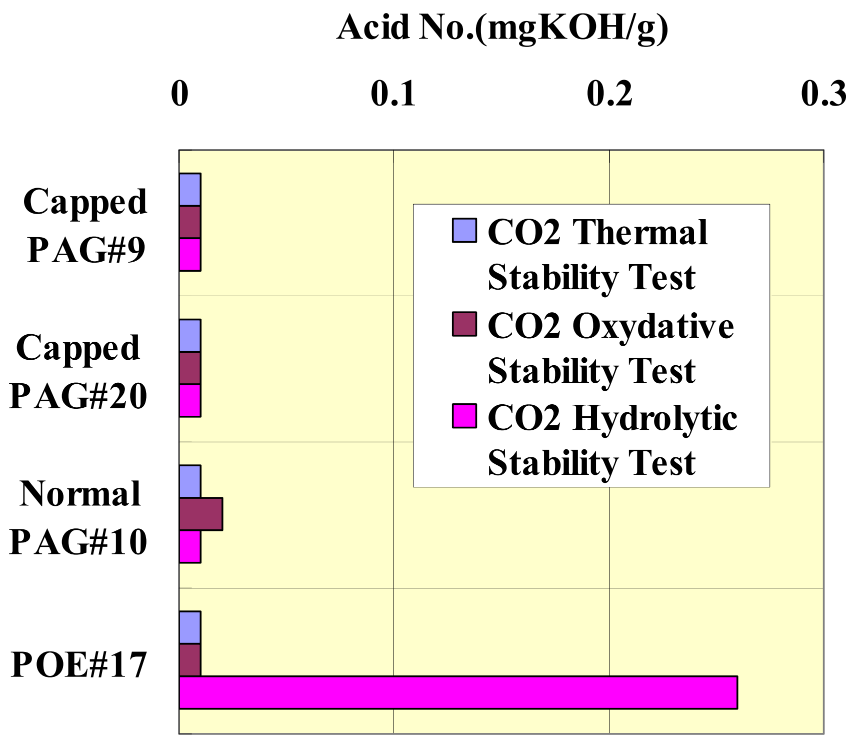
		Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#17
Appearance	Oil	Good	Good	Good	Good
	Cat□	Good	Good	Good	Fe→black
Acid No.(mgKOH/g)		0.01	0.01	0.01	0.01

CO2 Oxidative Stability Test

		Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#17
Appearance	Oil	Good	Good	Good	Good
	Cat□	Good	Good	Good	Fe→black
Acid No.(mgKOH/g)		0.01	0.01	0.02	0.01

CO2 Hydrolytic Stability Test

		Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#17
Appearance	Oil	Good	Good	Good	Good
	Cat□	Good	Good	Good	Fe→black
Acid No.(mgKOH/g)		0.01	0.01	0.01	0.26



POE

Hydrolysis RCOOR +□H_2O →□RCOOH + HOR

Reaction with Iron RCOOR +□Fe →□Fe(Black Surface)

Comparison with PAGs and POE of Catalyst in Autoclave Test

CO_2 Thermal Stability Test□Result

Capped PAG#9 | Capped PAG#20 | Normal PAG#10 | POE#17

Fe Cu Al

Stability of PAGs and POE with HFC152a

(R152a Sealed Tube Test Results)

R152a Thermal Stability Test

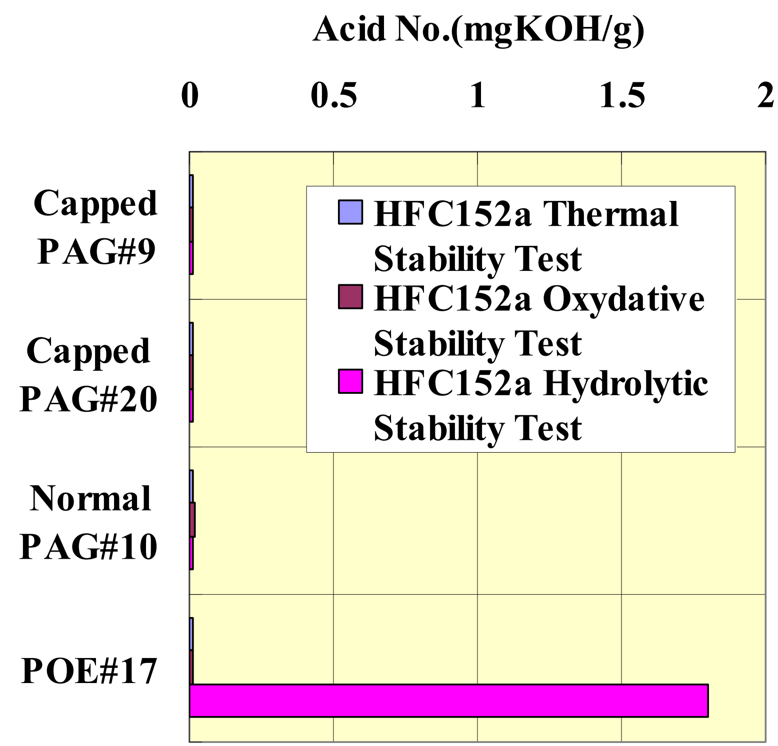
		Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#170
Appearance	Oil	Good	Good	Good	Good
	Cat	Good	Good	Good	Fe→gray
Acid No.(mgKOH/g)		0.01	0.01	0.01	0.01

R152a Oxidative Stability Test

		Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#170
Appearance	Oil	Good	Good	Good	Good
	Cat	Good	Good	Good	Fe→gray
Acid No.(mgKOH/g)		0.01	0.01	0.02	0.01

R152a Hydrolytic Stability Test

		Capped PAG#9	Capped PAG#20	Normal PAG#10	POE#170
Appearance	Oil	Good	Good	Good	Good
	Cat	Good	Good	Good	Fe→ black
Acid No.(mgKOH/g)		0.01	0.01	0.01	1.8

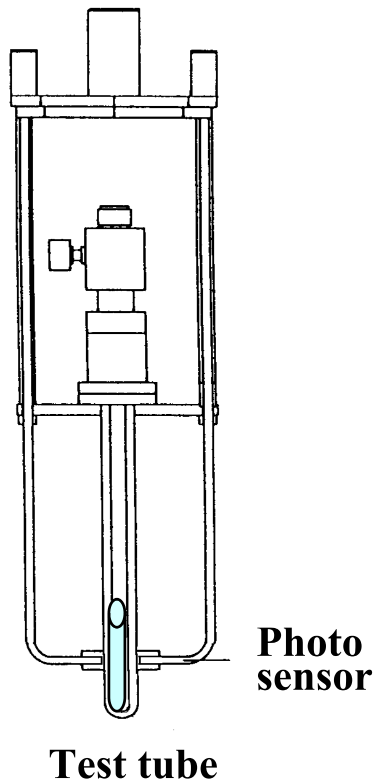


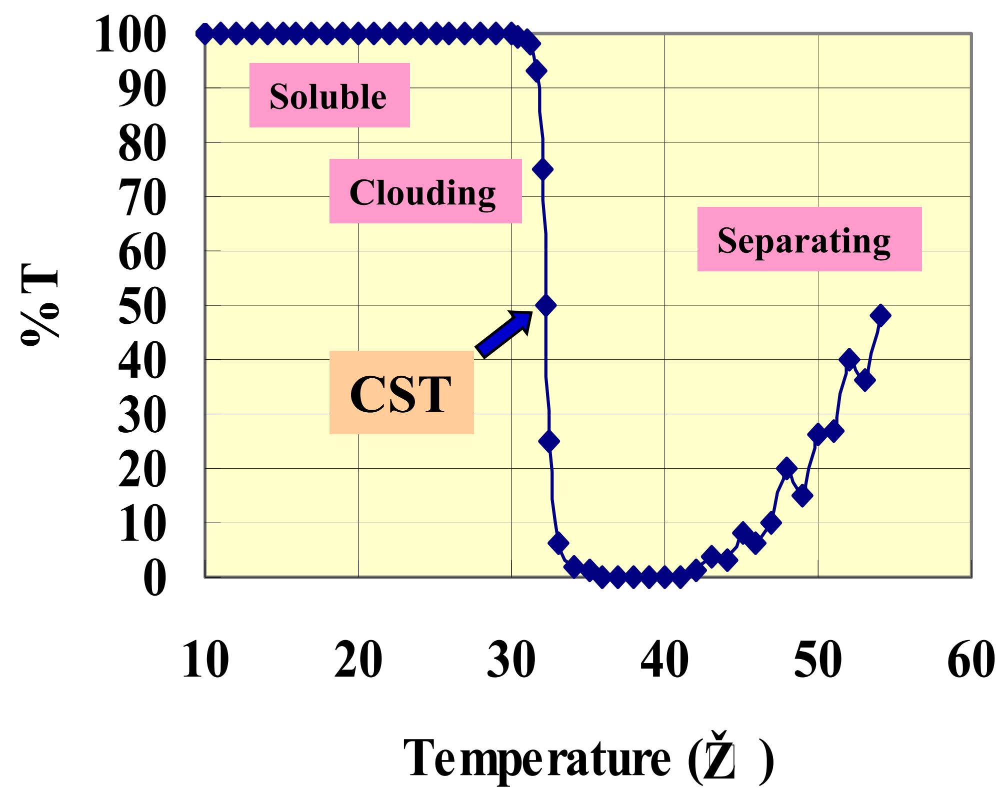
Capped-PAG, Normal-PAG : Good Stability

POE : Poor Stability (Hydrolysis and Reaction with Iron)

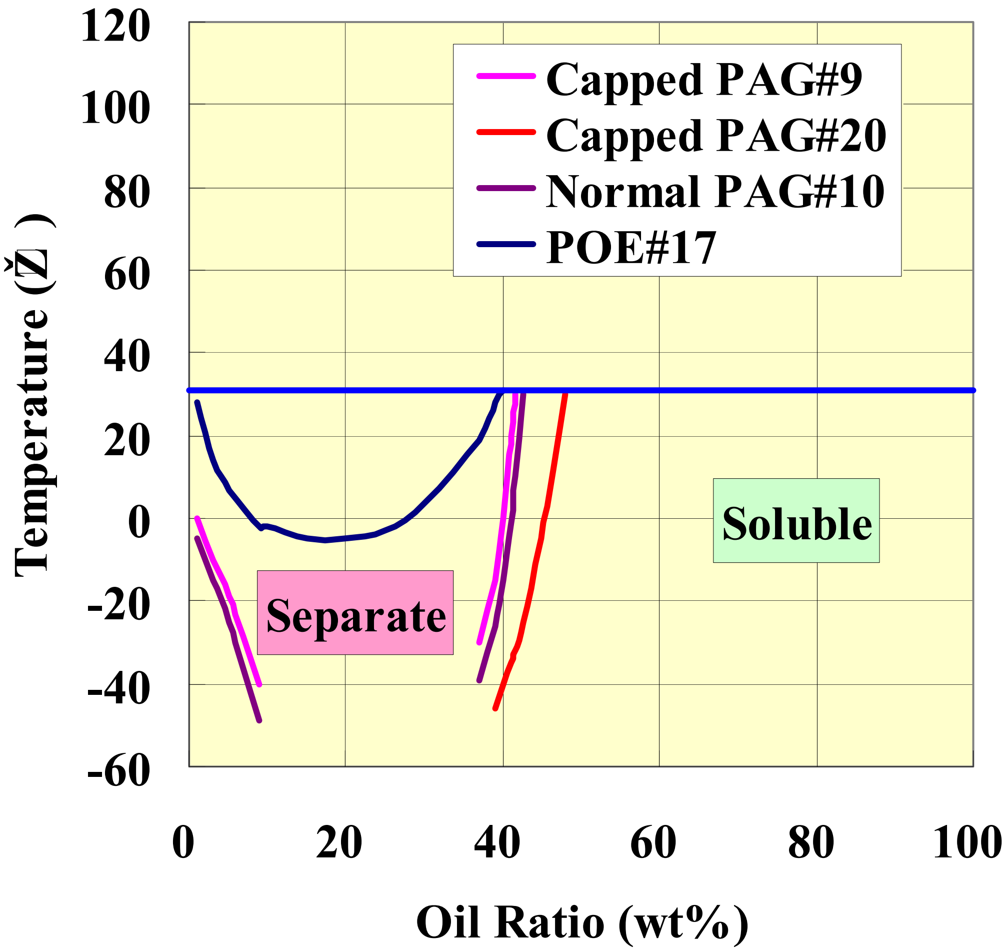
Miscibility of PAGs and POE

(Test Apparatus and Method)

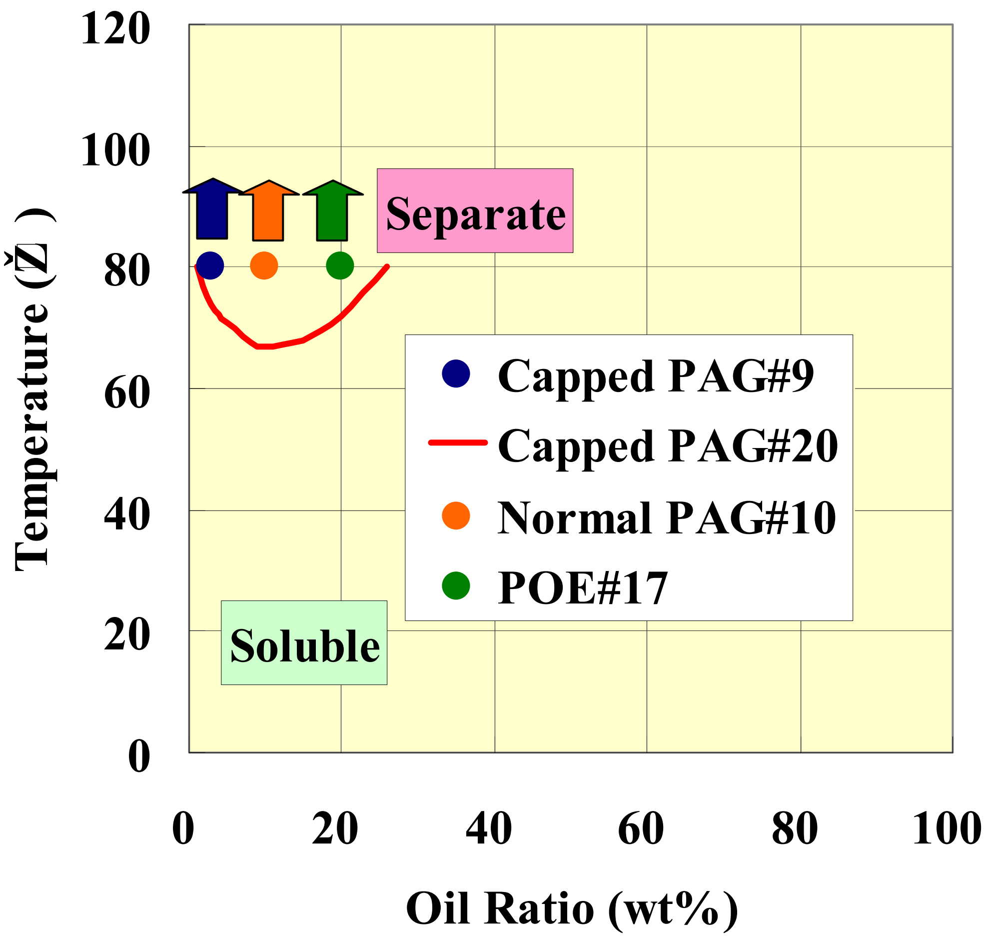




Miscibility of PAGs and POE with CO_2



Miscibility of PAGs and POE with HFC152a



Miscibility of PAGs and POE with CO_2 and HFC152a

Good ←□Miscibility□→□Poor

POE□□□Capped-PAG □ Normal-PAG

Assignment

□Supercritical-CO_2 : Poor Miscibility

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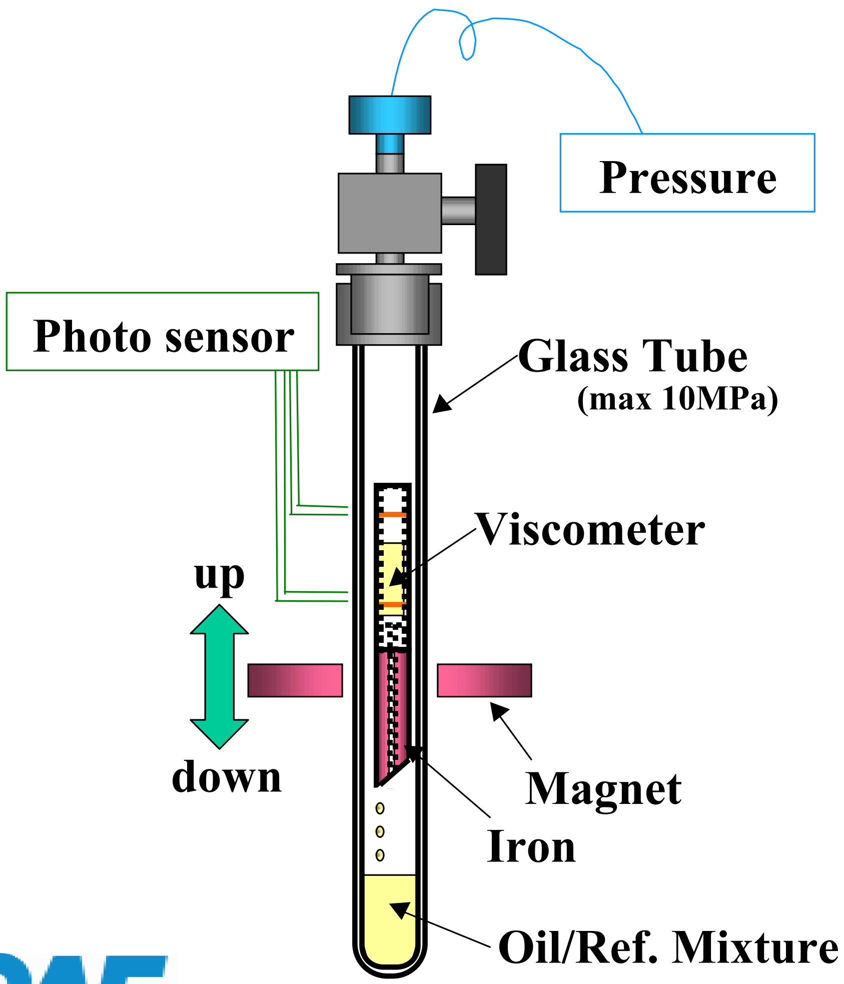
Mixture Viscosity of Oil/Refrigerant

(Test Apparatus and Method)



Hermetic Type Viscometer

□Viscosity

□Solubility

@constant Temp./Pressure

The Solubility(Xr) is determined as follows :

$$Xr = (Wr - dVg) \square (Wo + Wr - dVg)$$

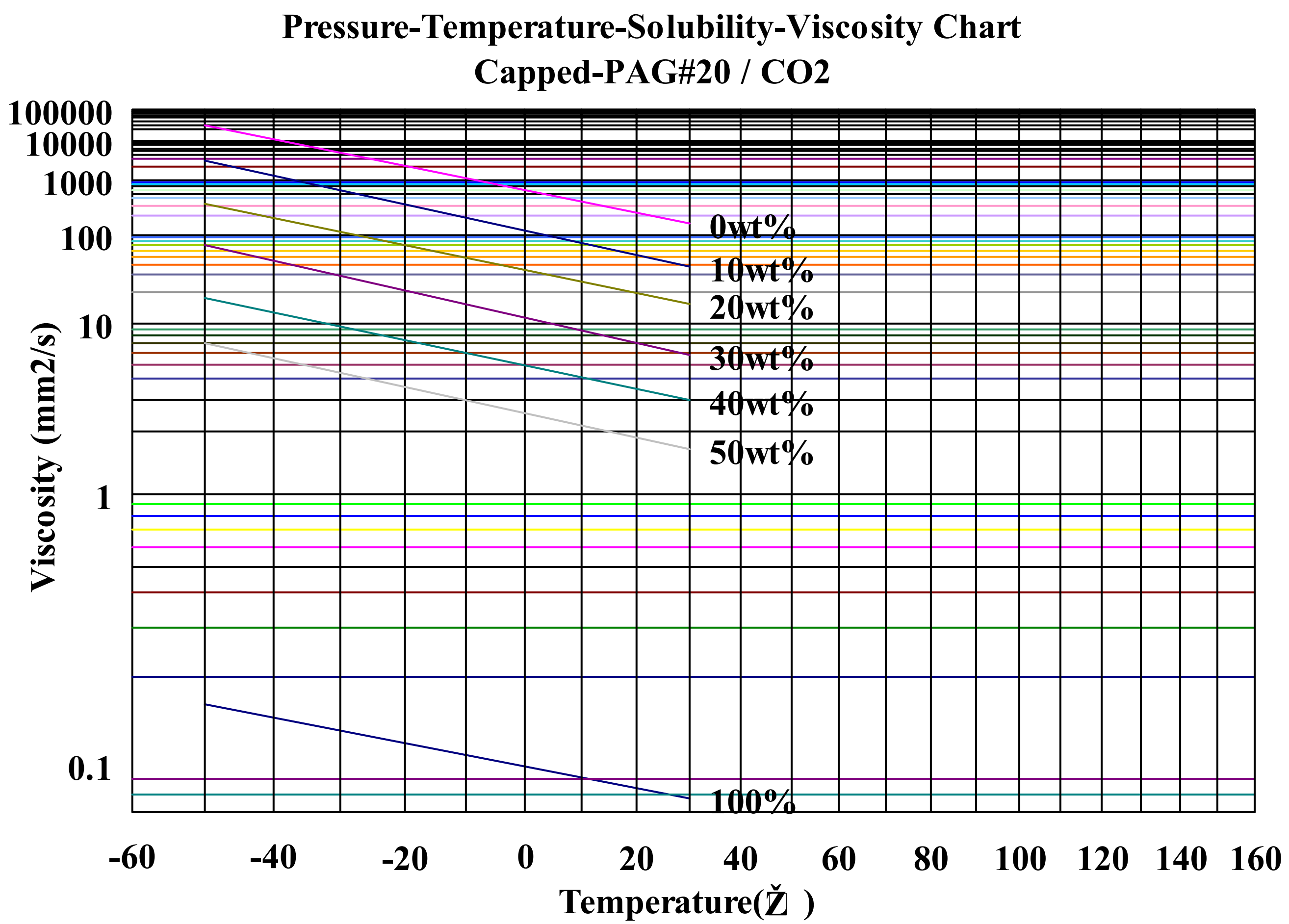
Wo□; the mass of oil

Wr ; the mass of refrigerant

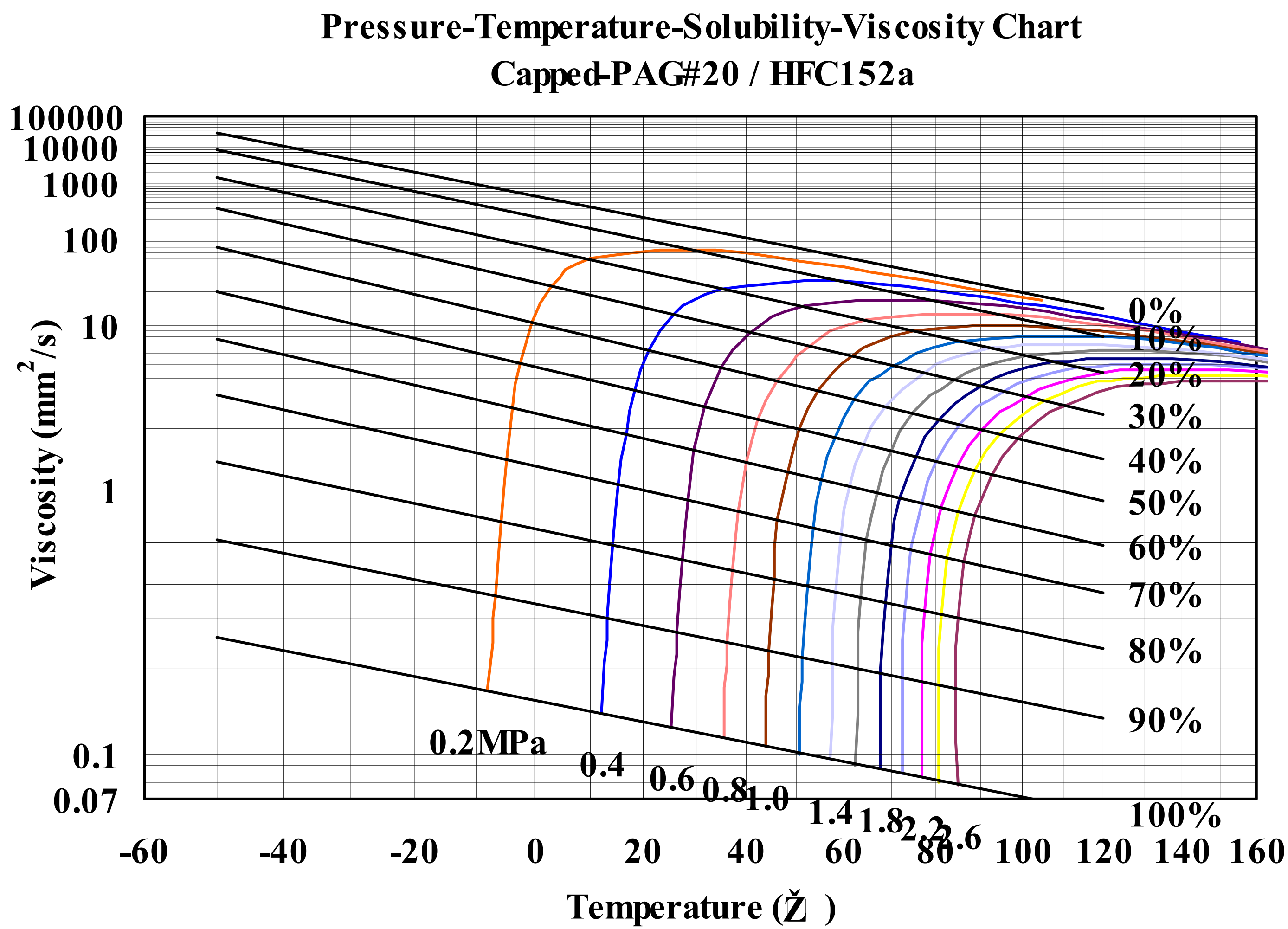
d ; the refrigerant vapor density

Vg ; gas volume at the experimental temperature

Mixture Viscosity of PAG with CO_2

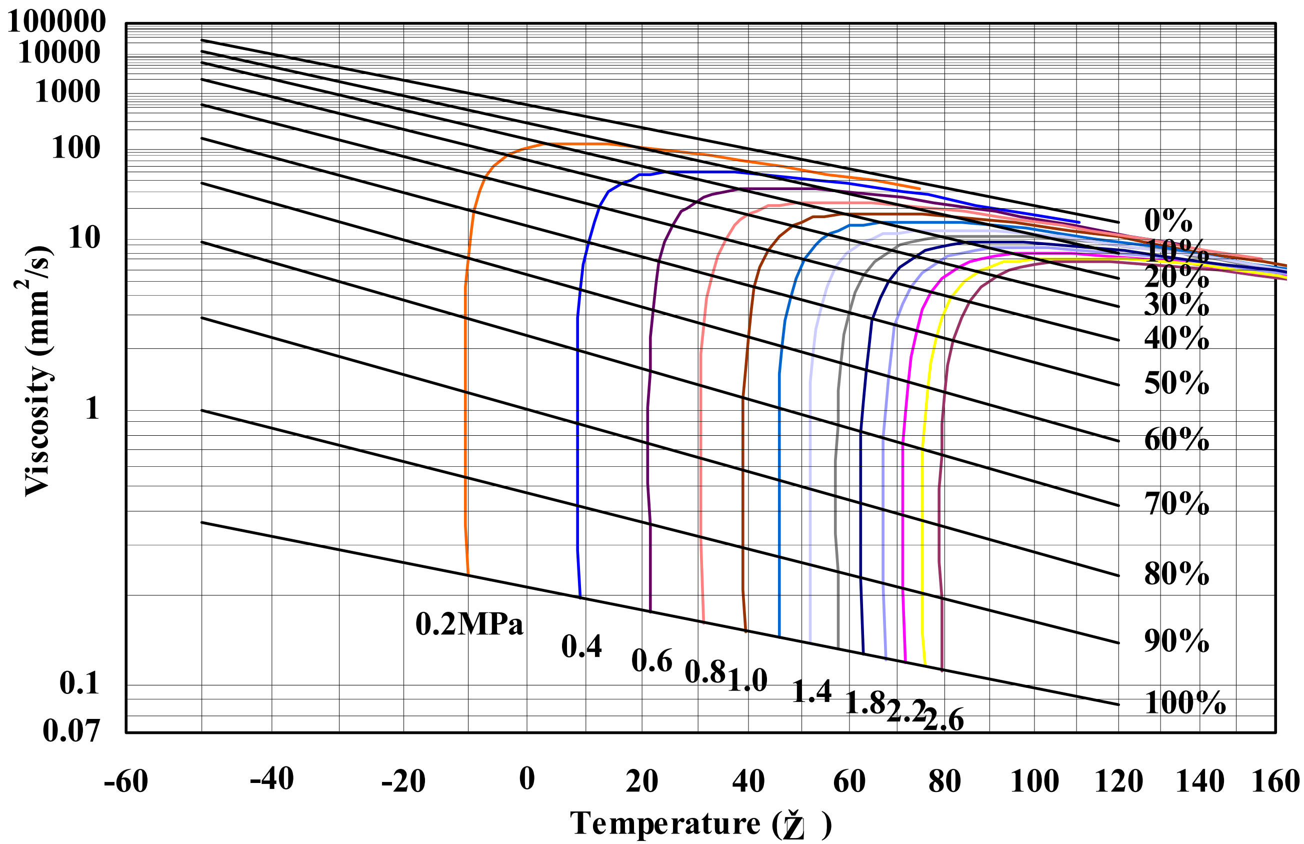


Mixture Viscosity of PAG with HFC152a



Mixture Viscosity of PAG with HFC134a

Pressure-Temperature-Solubility-Viscosity Chart
Capped-PAG#20 / HFC134a



Mixture Viscosity of PAG with CO_2 and HFC152a

Mixture Viscosity at 0□

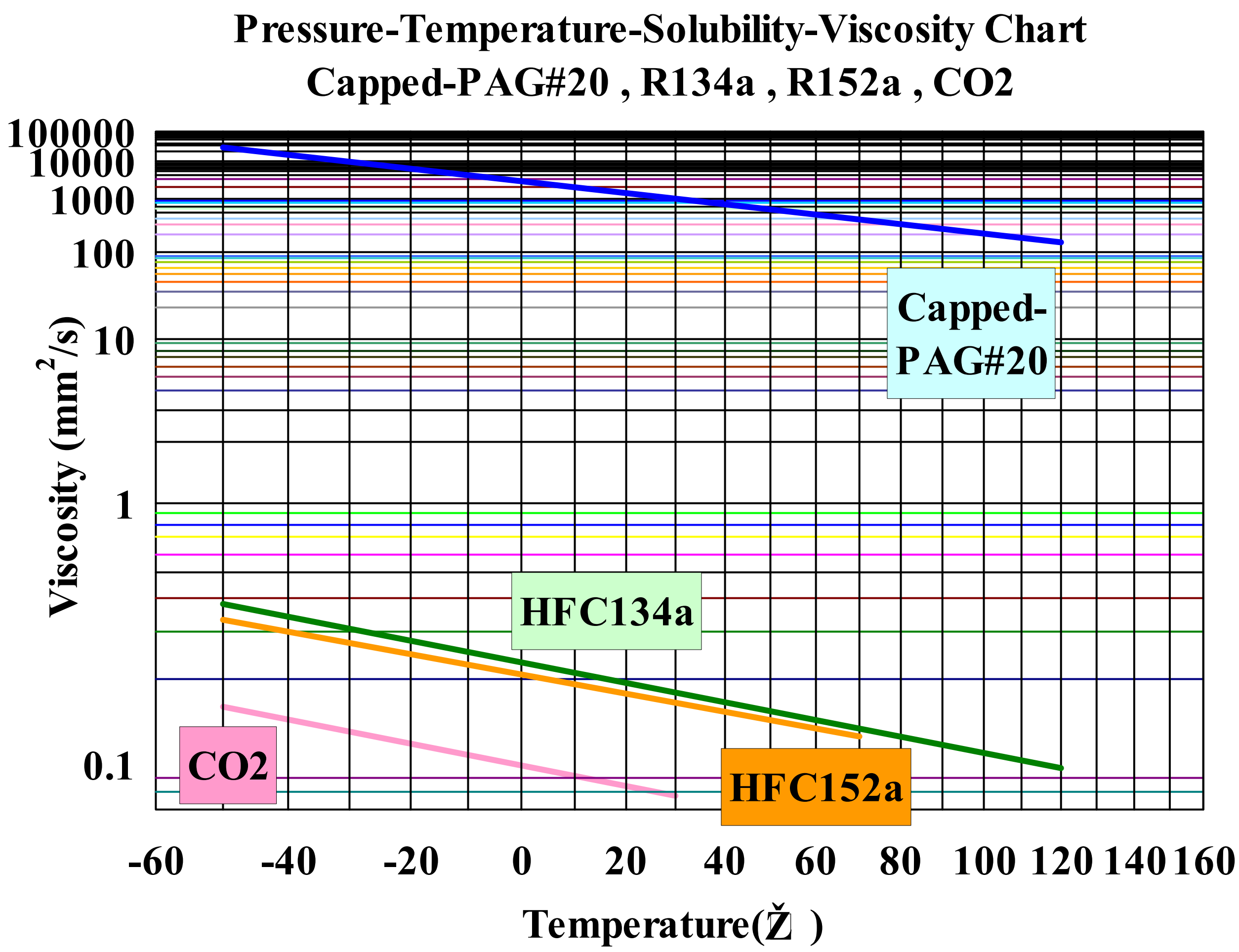
CO_2 / Capped-PAG#20 Ratio = 20 / 80

	HFC134a	HFC152a	CO_2
Viscocity (mm^2/s)	160	70	35

Mixture Viscosity □□ PAG HFC134a □ PAG HFC152a □ PAG CO_2

□Depend on Refrigerant Viscosity & Structure

Viscosity of HFC134a , HFC152a and CO_2



Molecular Structure of HFC134a , HFC152a and CO_2

	HFC134a	HFC152a	CO_2
	H F │ │ H-C-C-F │ │ F F	H H │ │ H-C-C-F │ │ H F	O=C=O
Molecular Weight	102	66	44

High ← Viscosity → Low

Miscibility and Mixture Viscosity

Requirement

Miscibility of Oil with Supercritical-CO_2

Most suitable Viscosity of Oil with CO_2, HFC152a

→□Capped-PAG#9,#15,#20

Conclusion(1)

Capped-PAG□Good Chemical Structure (σ-Bonding)

$$CH_3\text{-}O\text{-}(\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}O)_m\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$$

Normal PAG(HO-group) : pKa, Poor Lubricity

POE (π-Bonding) : Hydrolysis,Tribochemical Reaction

Conclusion(2)

Capped-PAG for Automotive A/C with CO_2 and HFC152a

□Good Specification of VI(Viscosity-Temp. Property)

□Good Lubricity(Seizure,Wear,Fatigue Life)

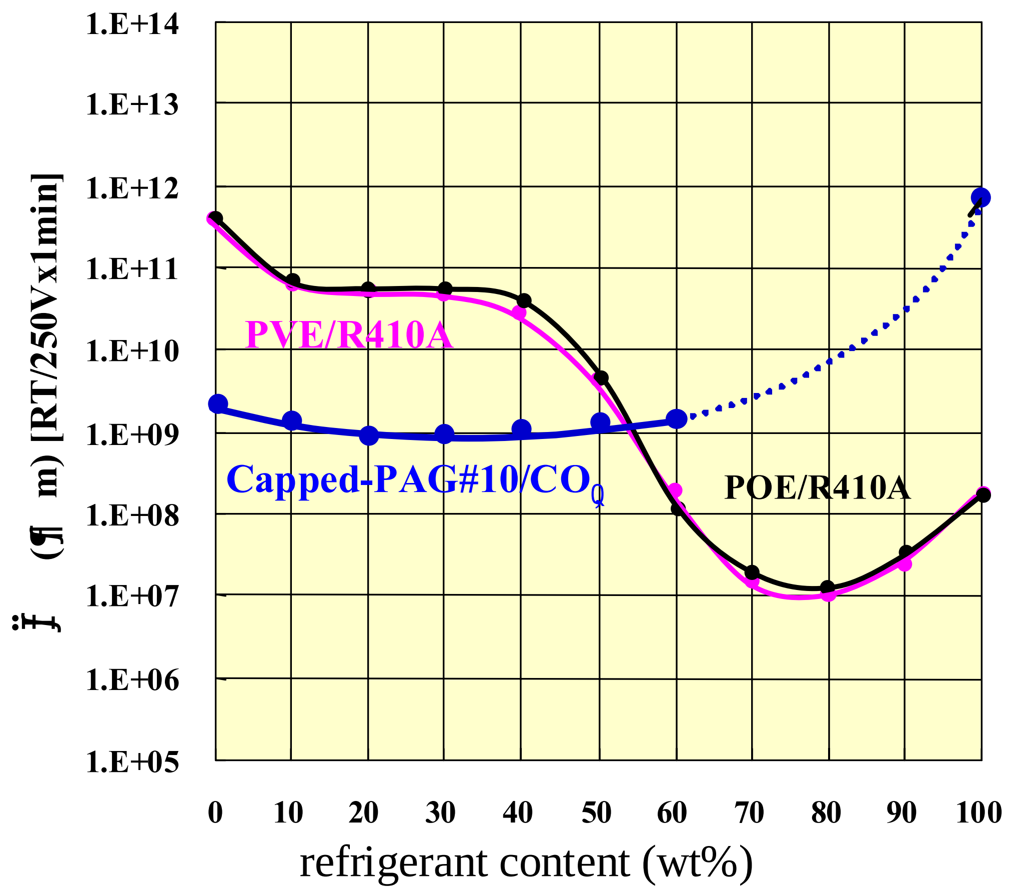
□Good Stability

□ **Most suitable Viscosity for CO_2 and HFC152a**

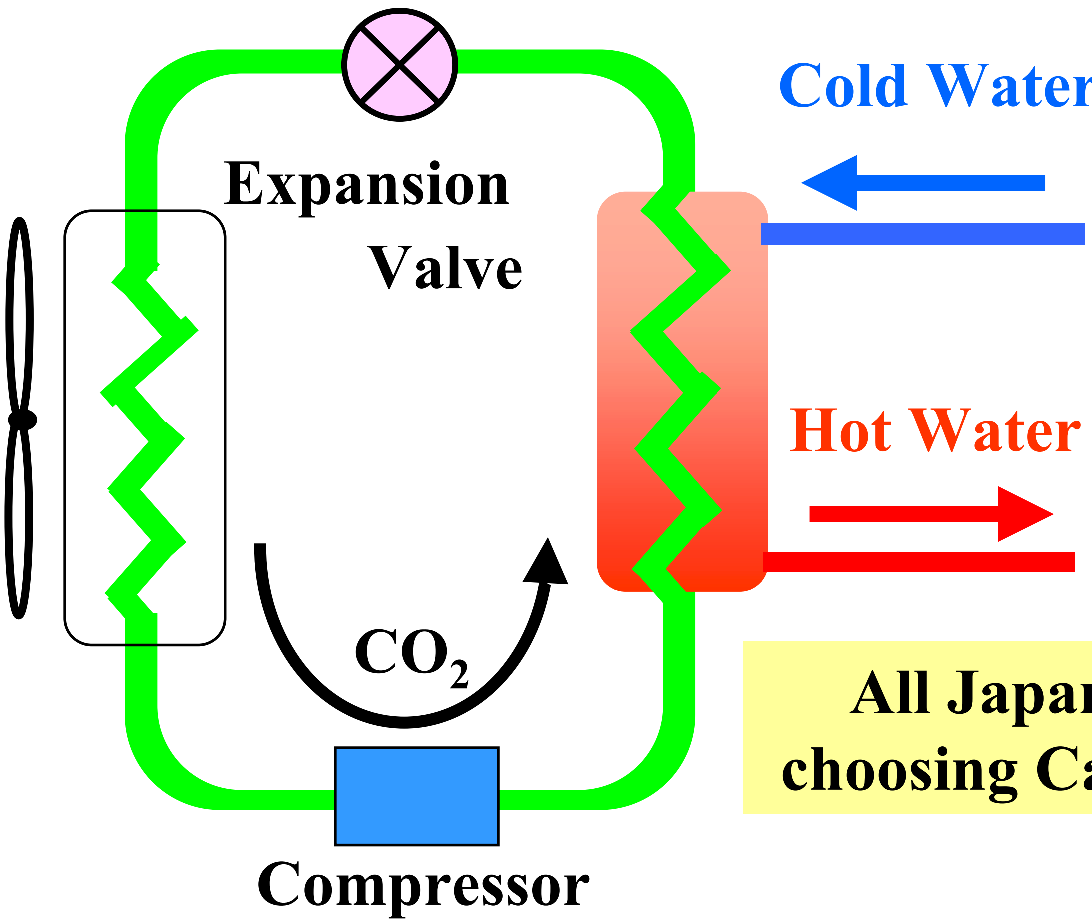
→ Capped-PAG#9, #15,#20 □□

Approval of Capped-PAGs for Hermetic Compressors with CO_2

Volumetric Resistivity of Capped-PAG with CO_2

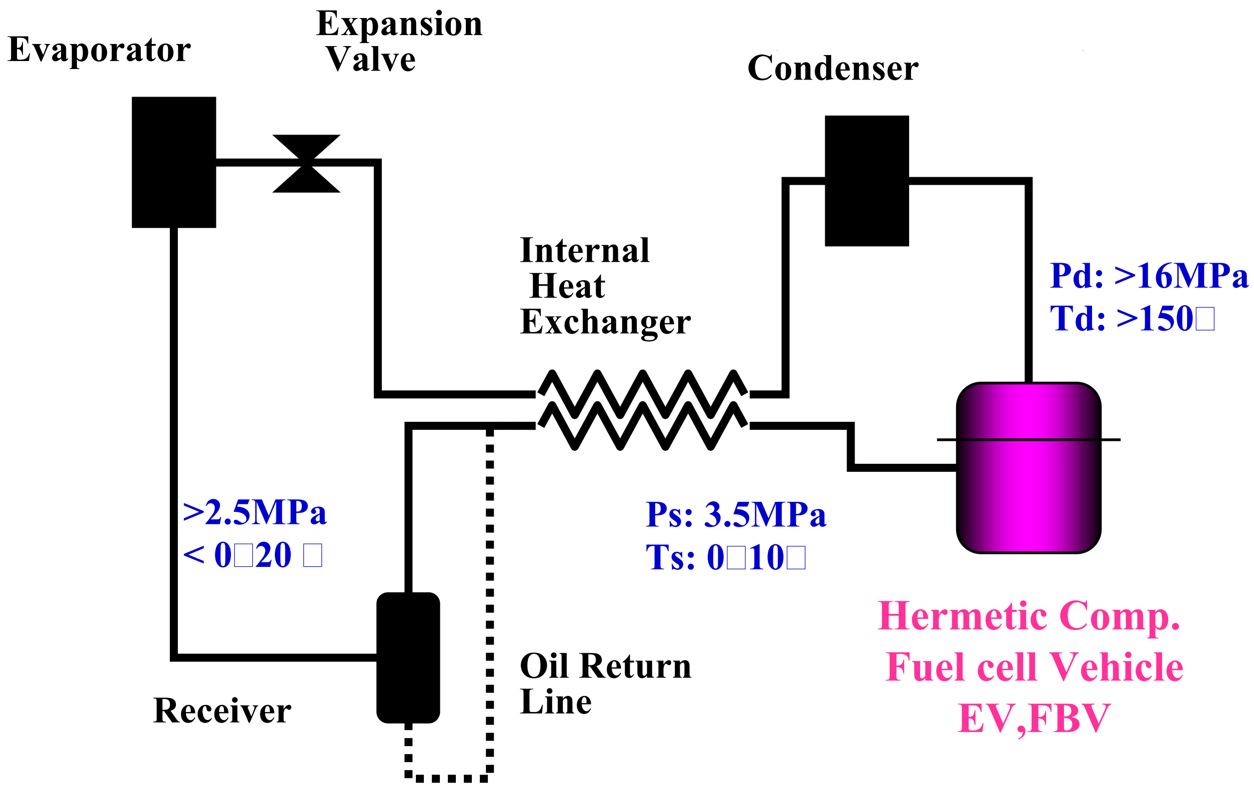


(1) CO_2 Heat Pump Water Heater System[35] with Capped-PAG



All Japanese OEM's are choosing Capped-PAG#9,#20

(2)CO_2 A/C System for Fuel cell Vehicle with Capped-PAG



Japanese OEM's

are choosing Capped-PAG#9

Conclusion(3)

Capped-PAGs have been used for

- □ CO_2 Heat Pump Water Heater System
- □ CO_2 A/C System for Hybrid Vehicle
- □ CO_2 Vending machine, Showcase

In the near future

- □Automotive A/C with CO_2 and HFC152a

Next time (for HFC410A Substitution)

- □ CO_2 Air Conditioner(PAC,RAC)