Evaluation of Lubricants for a Carbon Dioxide Automobile A/C system

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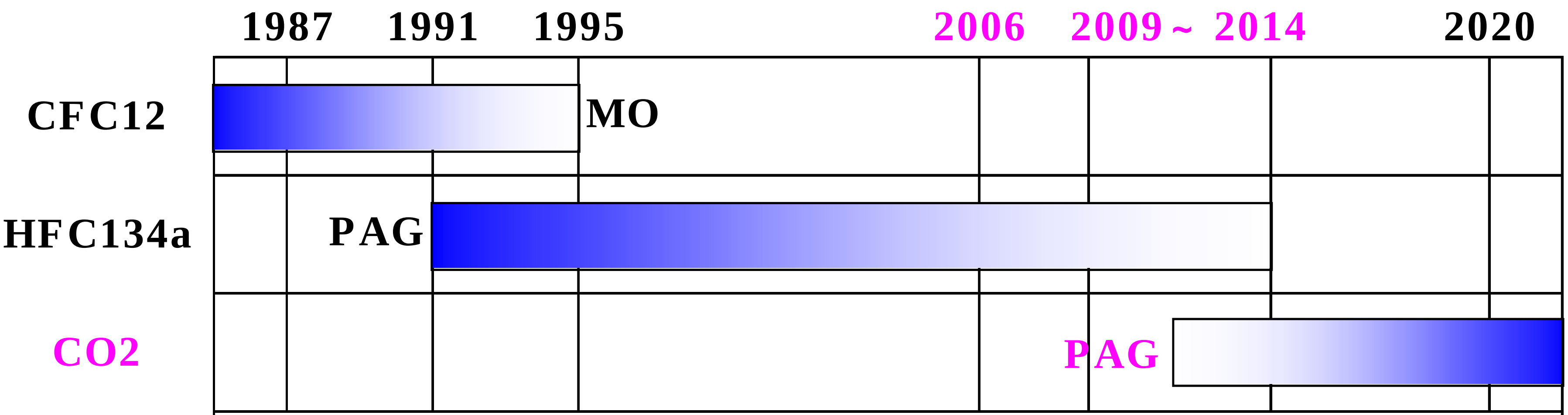
The Trend of the Refrigerating Oils for CO_2



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

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

2020 : end of HCFC

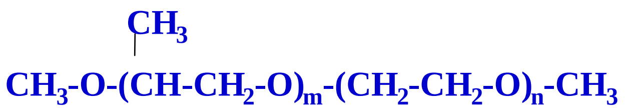
Chemical Structure of PAG

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

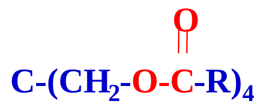
- **Main Chain : Good Stability and No Hydrolysis**
- **End Cap : Good Lubricity and Solubility**
- **Free Design of m/n : Flexibility to alter Miscibility**
- **Free Design of m+n : Flexibility to alter Viscosity**

Comparison with PAG and POE of Bonding Energy

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



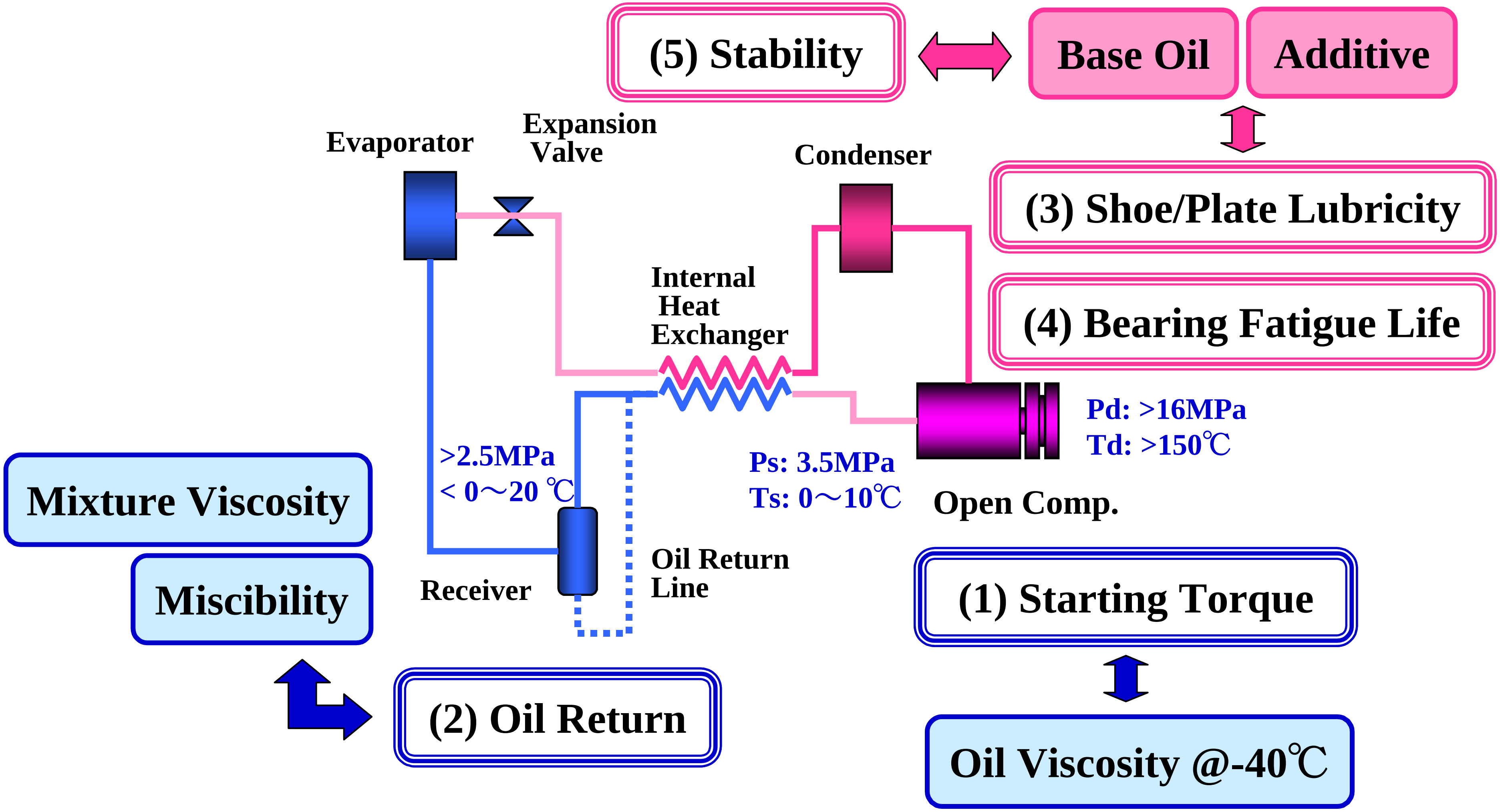
PAG



POE

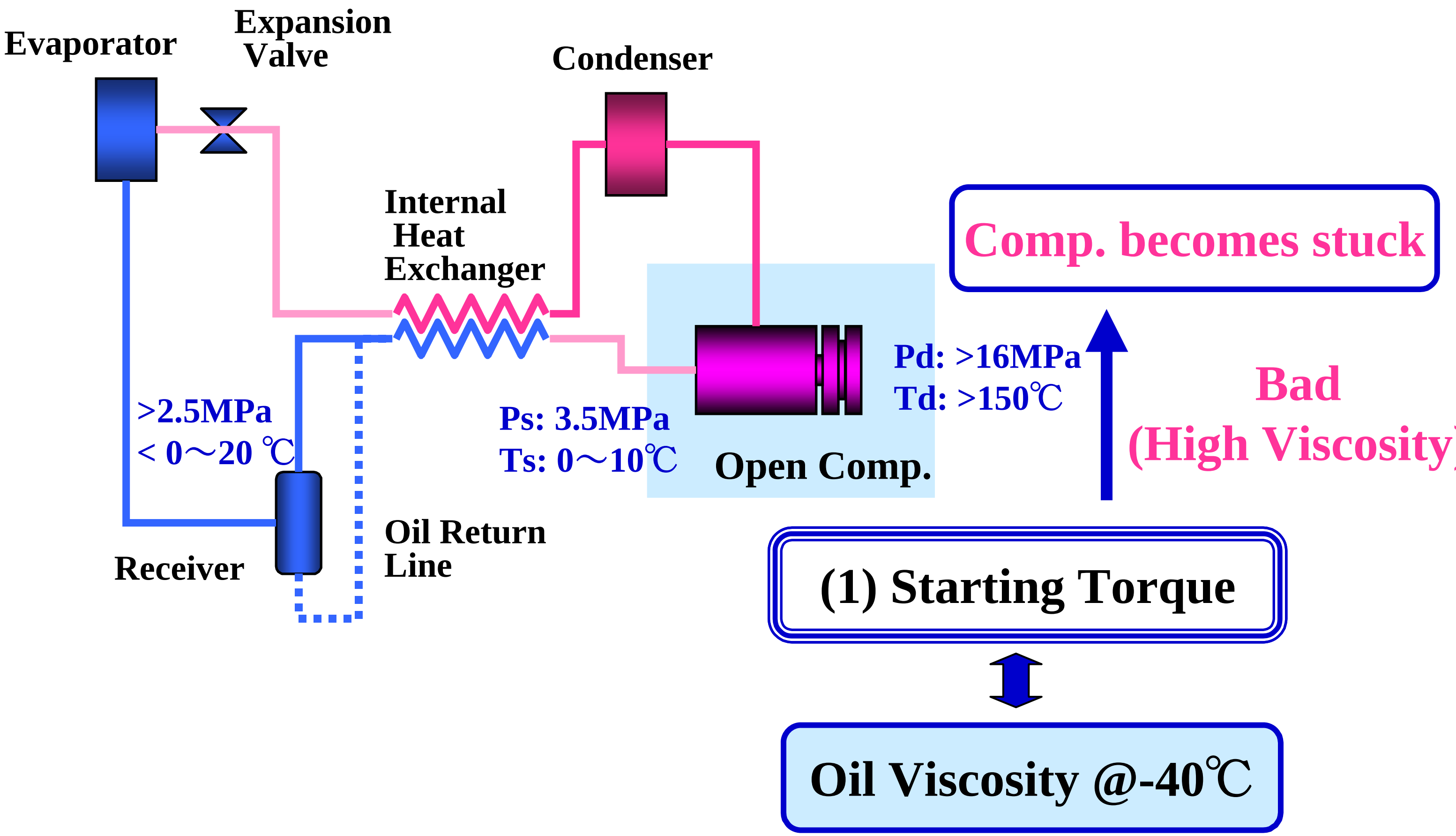
POE :π -Bonding → Hydrolysis , Tribochemical Reaction

Refrigerating Oil Requirement for CO_2 Automobile A/C System



(1) Starting Torque

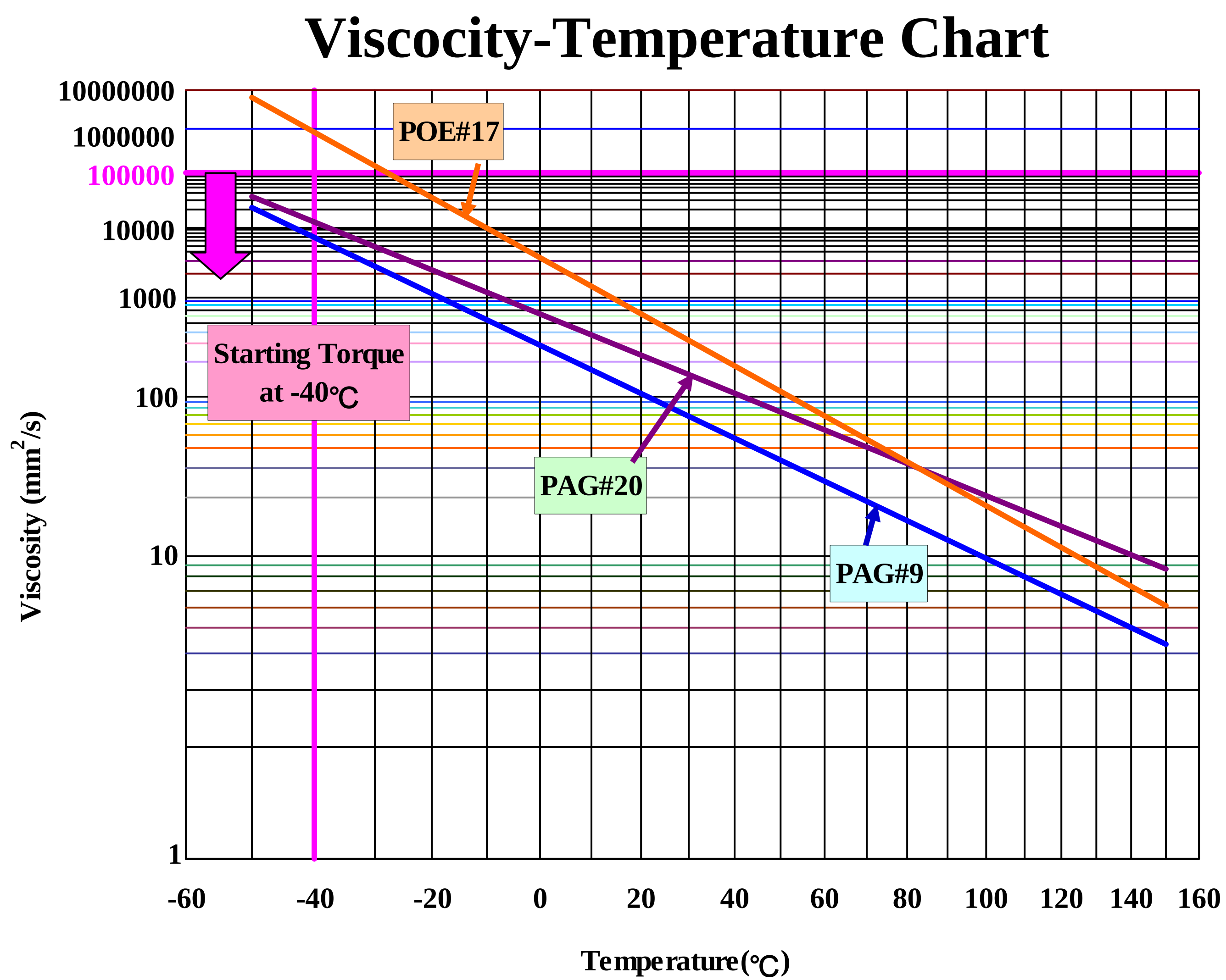
Lower viscosity is needed even under conditions of no Gas and low temp.



Viscosity(@-40℃) of PAG and POE

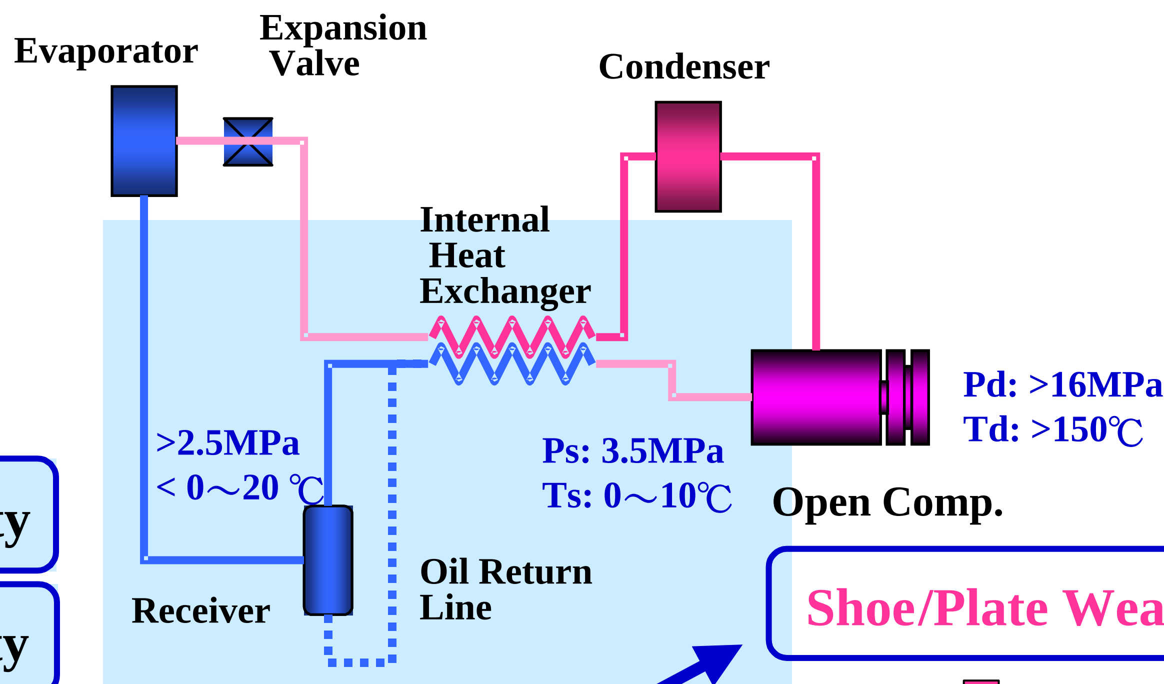
		PAG#9	PAG#20	POE#17
Viscosity(@ -40℃)	mm^2/s	6483	11600	774000
Viscosity(@100℃)	mm^2/s	9.234	20.01	17.13
Viscosity Index		203	225	109
Pour Point	℃	-45	-45	-32.5
Density(@15℃)	g/cm^3	0.9944	1.0195	0.9719
Acid Number	mgKOH/g	0.01	0.01	0.02

Viscosity (@-40℃) for Starting Torque of PAG and POE



(2) Oil Return

Property of Oil/CO_2 Mixture in Receiver



Mixture Viscosity

Miscibility

(2) Oil Return

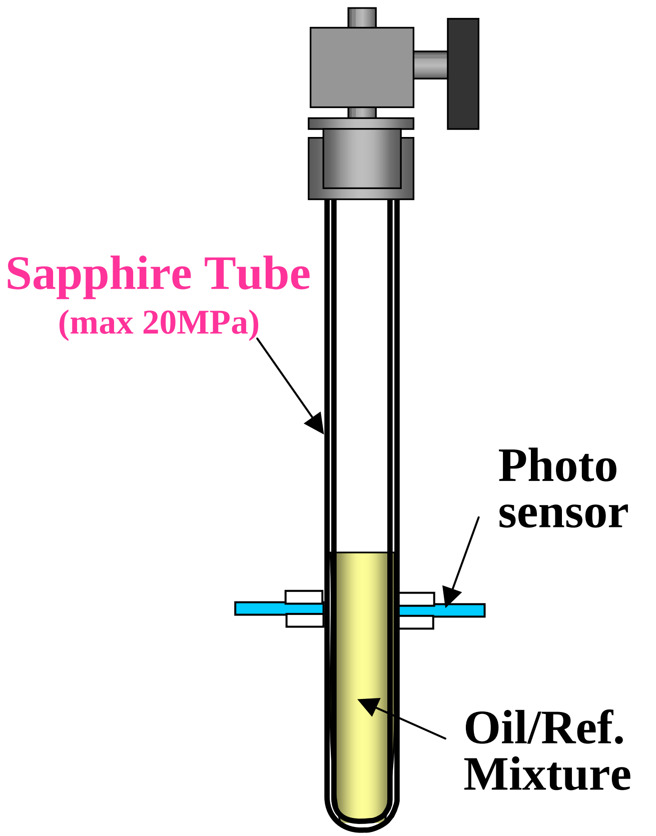
Bad

Shoe/Plate Wear

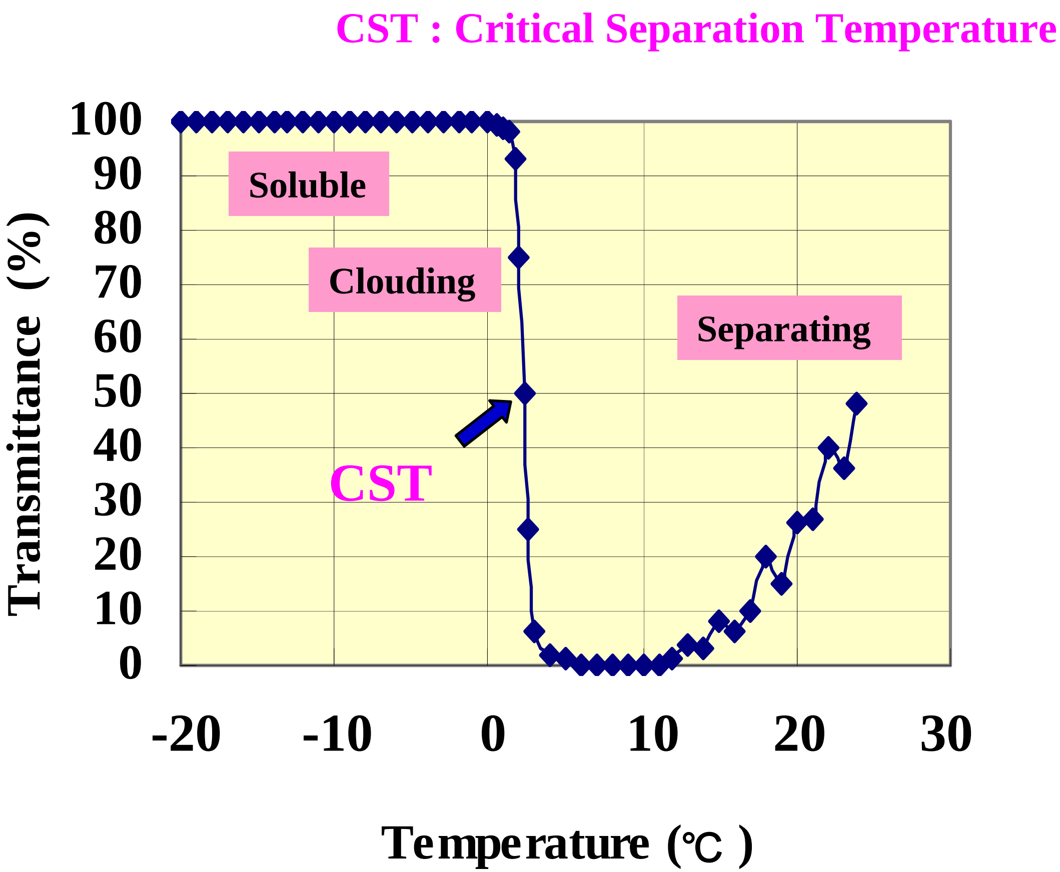
Need bypass line for Oil Return

Miscibility of Oil and Refrigerant

(Test Method)

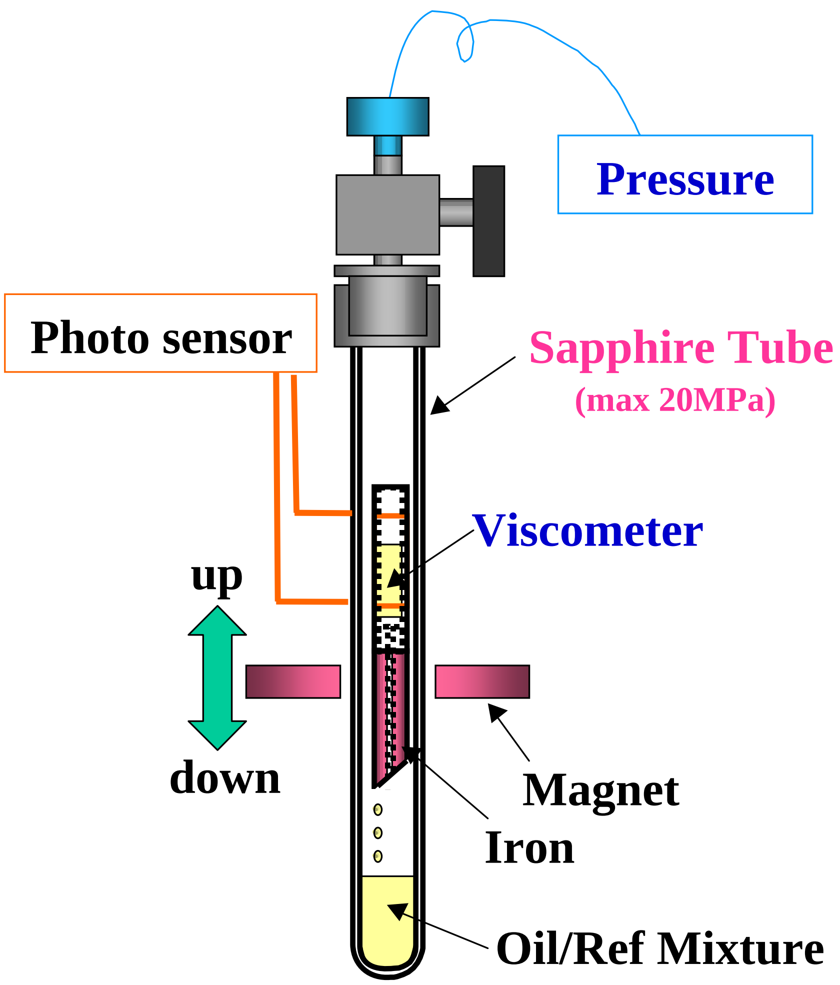


Miscibility Test Apparatus



Viscosity of Oil and Refrigerant Mixture

(Test Method)



Hermetic Type Viscometer

Detection and Calculation

- Viscosity
- Pressure
- Solubility

} at constant Temp.

Solubility (Xr) is determined as follows :

$$Xr = (Wr - dVg) / (Wo + Wr - dVg)$$

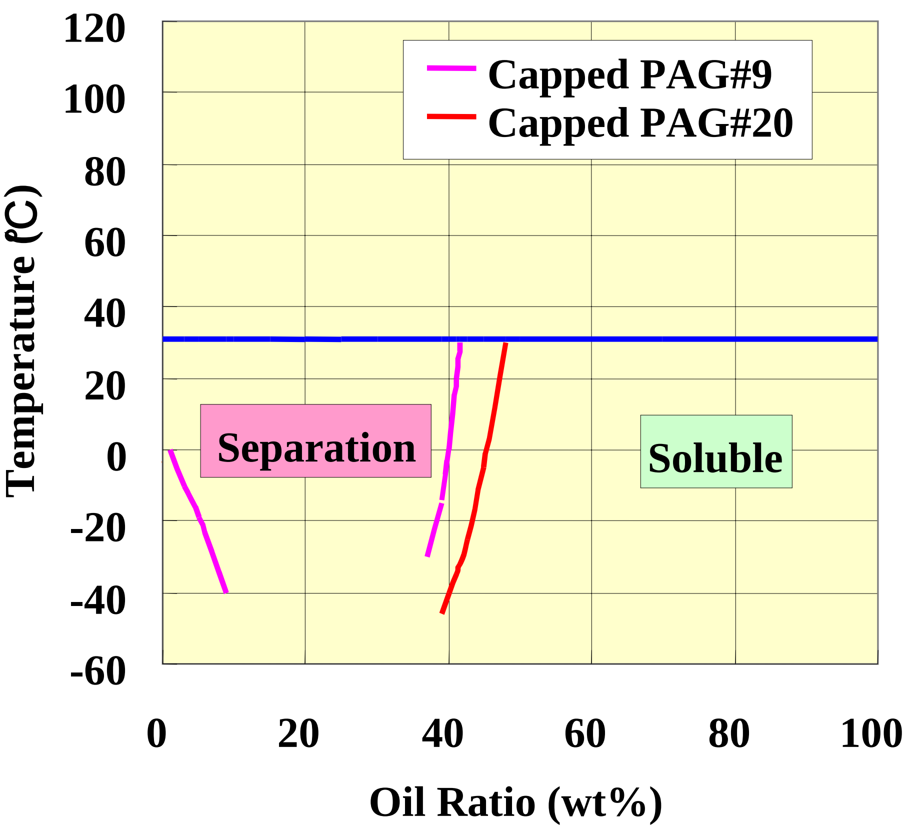
Wo ; the mass of oil

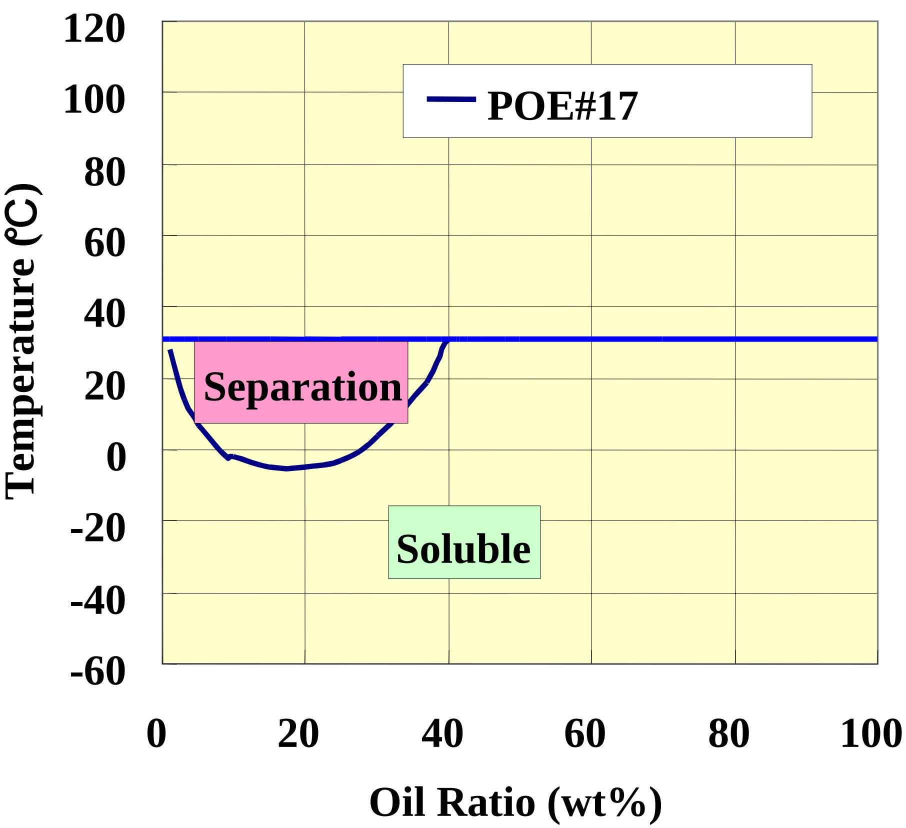
Wr ; the mass of refrigerant

d ; the refrigerant vapor density

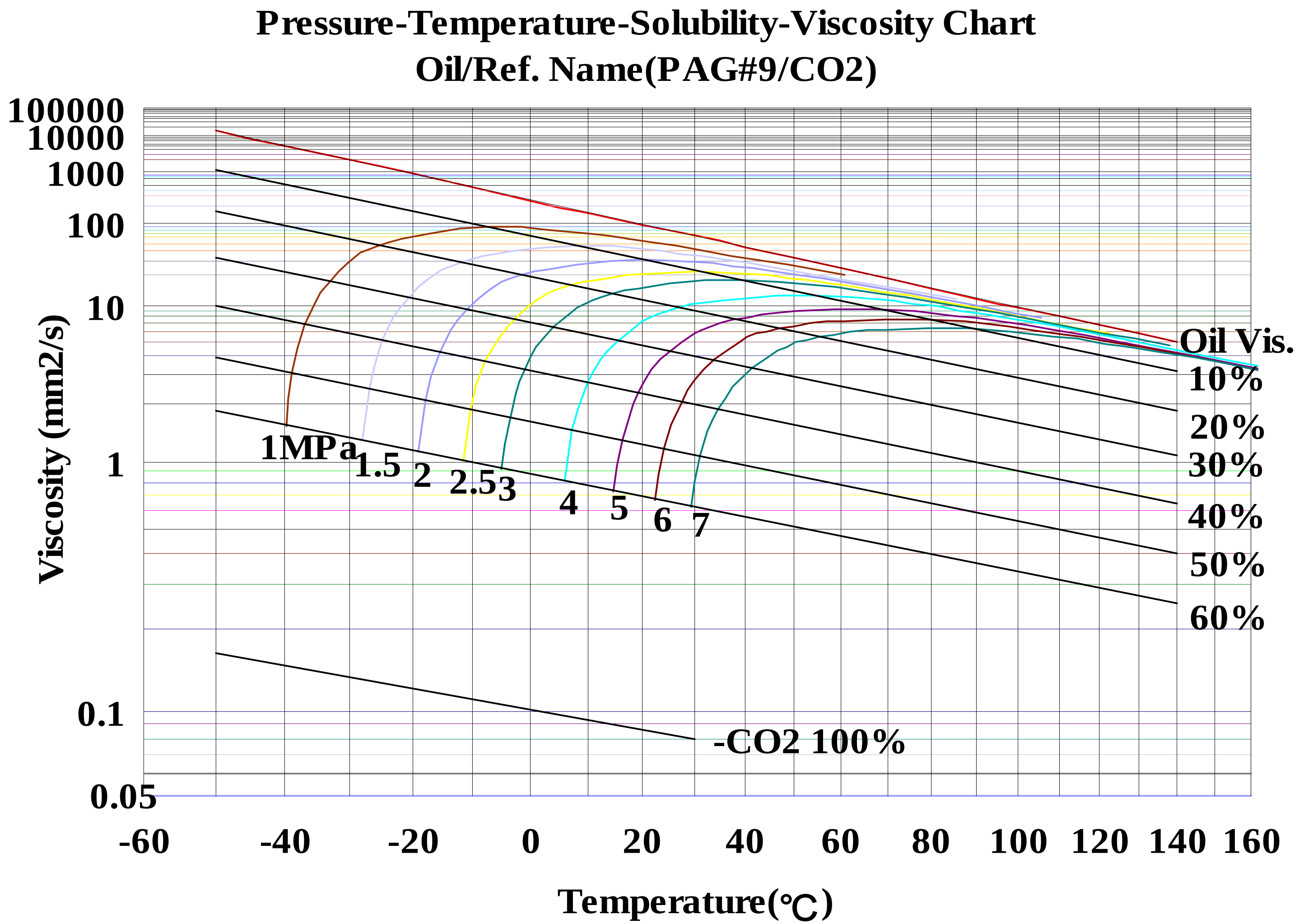
Vg ; gas volume at the experimental temperature

Miscibility of PAG and POE with CO_2

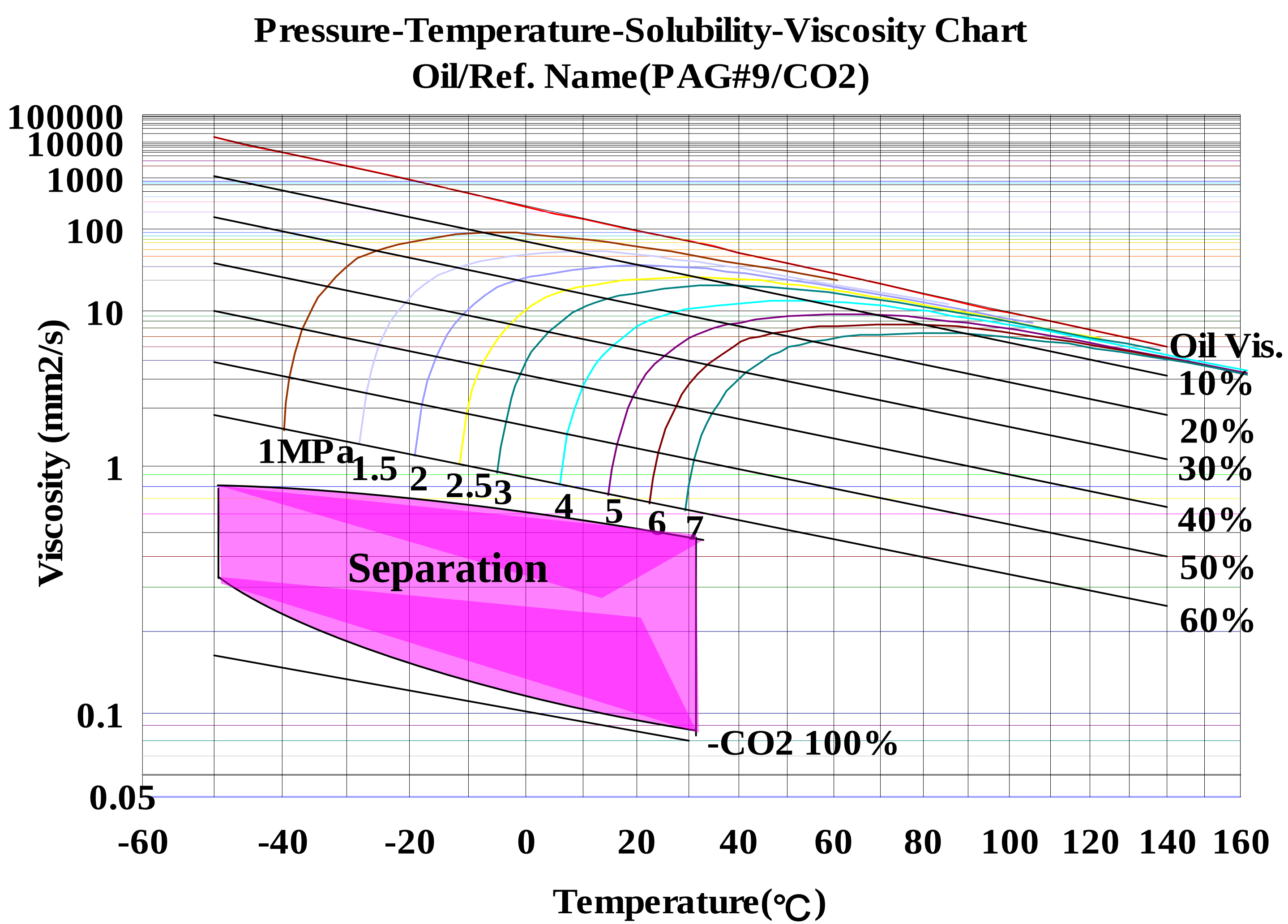




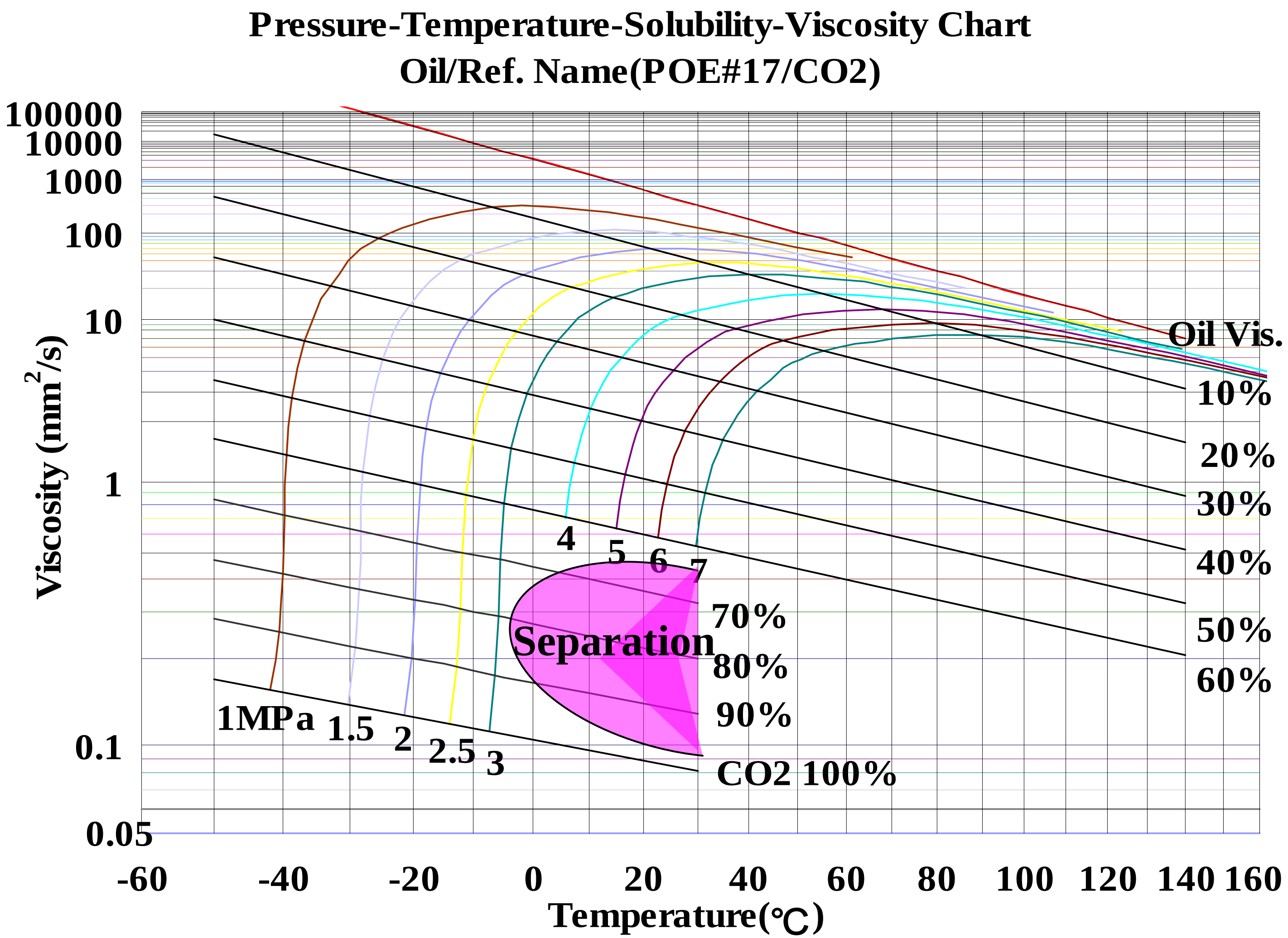
Viscosity of PAG and CO_2 Mixture



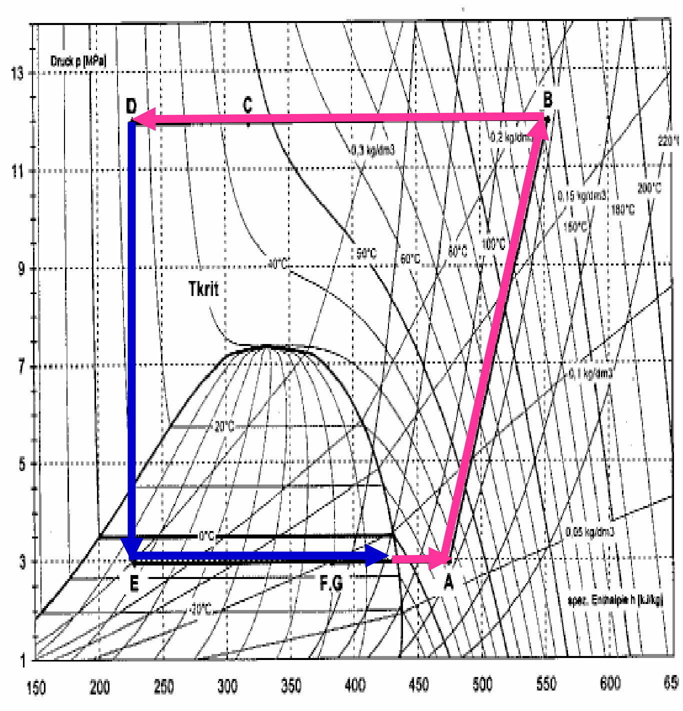
Viscosity of PAG/CO_2 Mixture and Immiscible Area



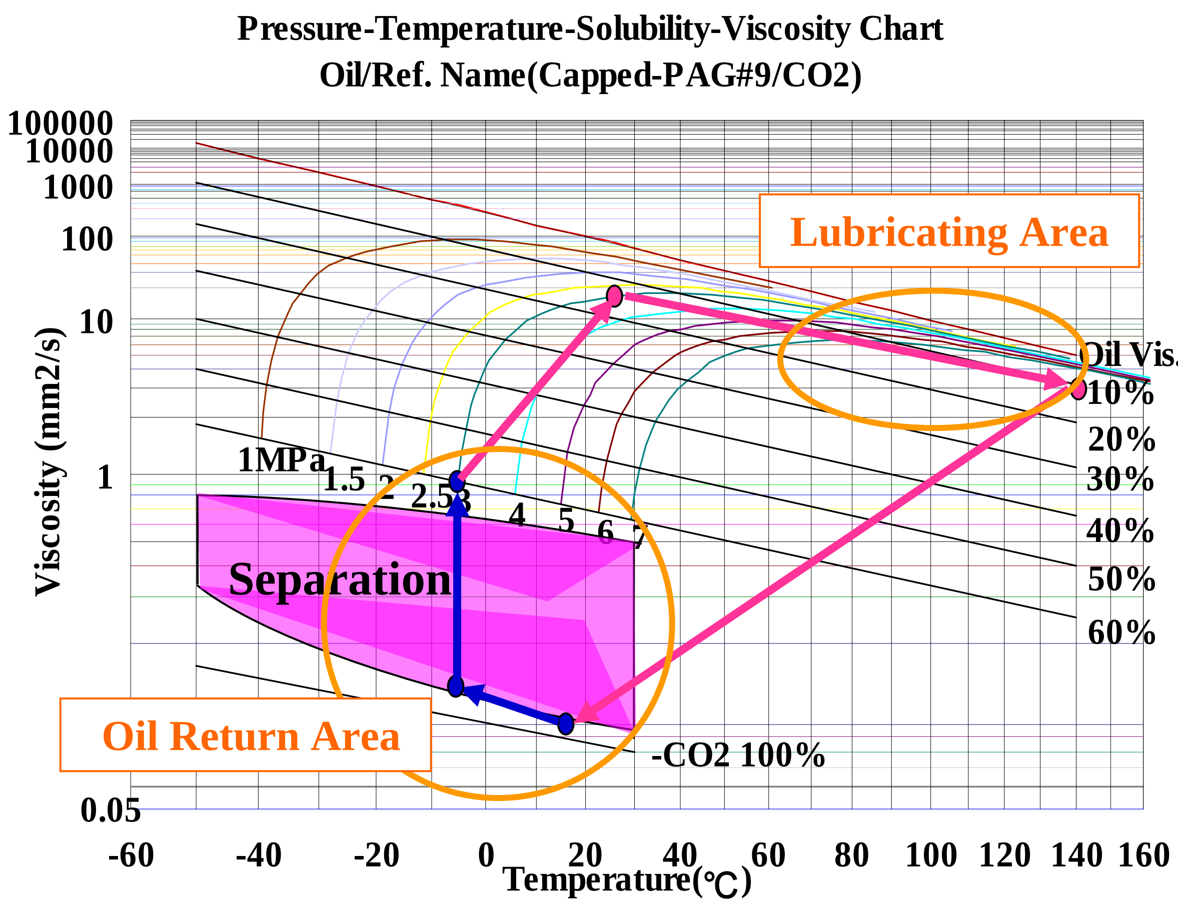
Viscosity of POE/CO_2 Mixture and Immiscible Area



Oil return property of PAG with CO_2

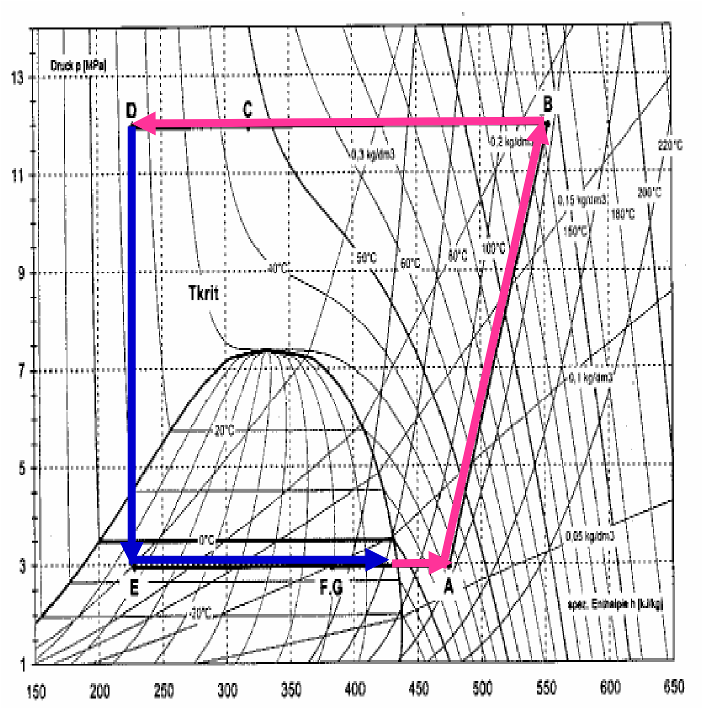


CO_2 P-h Diagram

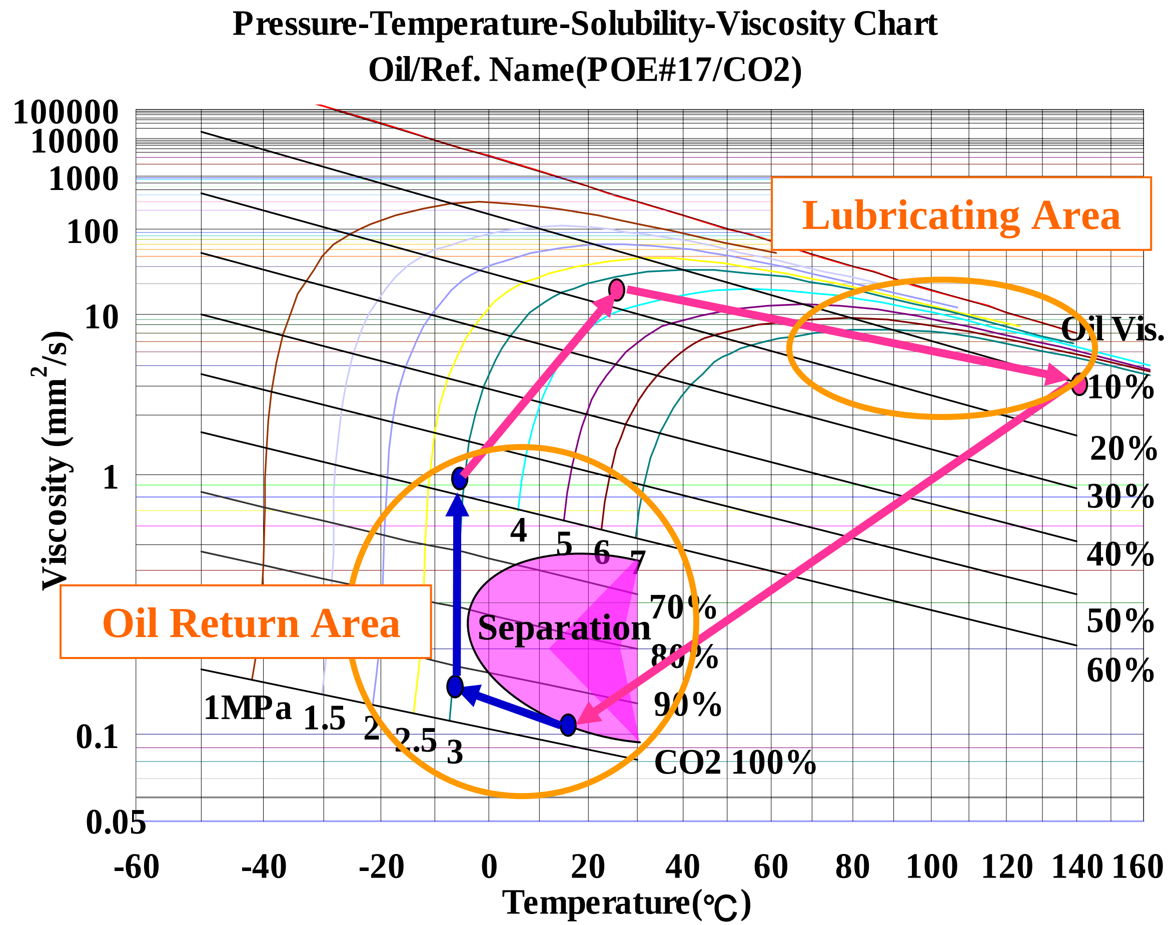


Viscosity-Temperature Chart

Oil return property of POE with CO_2



CO_2 P-h Diagram



Viscosity-Temperature Chart

Viscosity of PAG and CO_2 Mixture

Oil Return Area

	-5℃, 3MPa	
	Oil/CO2 (%)	Mixture Viscosity (mm^2/s)
PAG#9	37/63	0.9/0.12(Separate)
PAG#20	30/70	1.6/0.12(Separate)
POE#17	40/60	0.8

PAG

Need bypass line for Oil Return

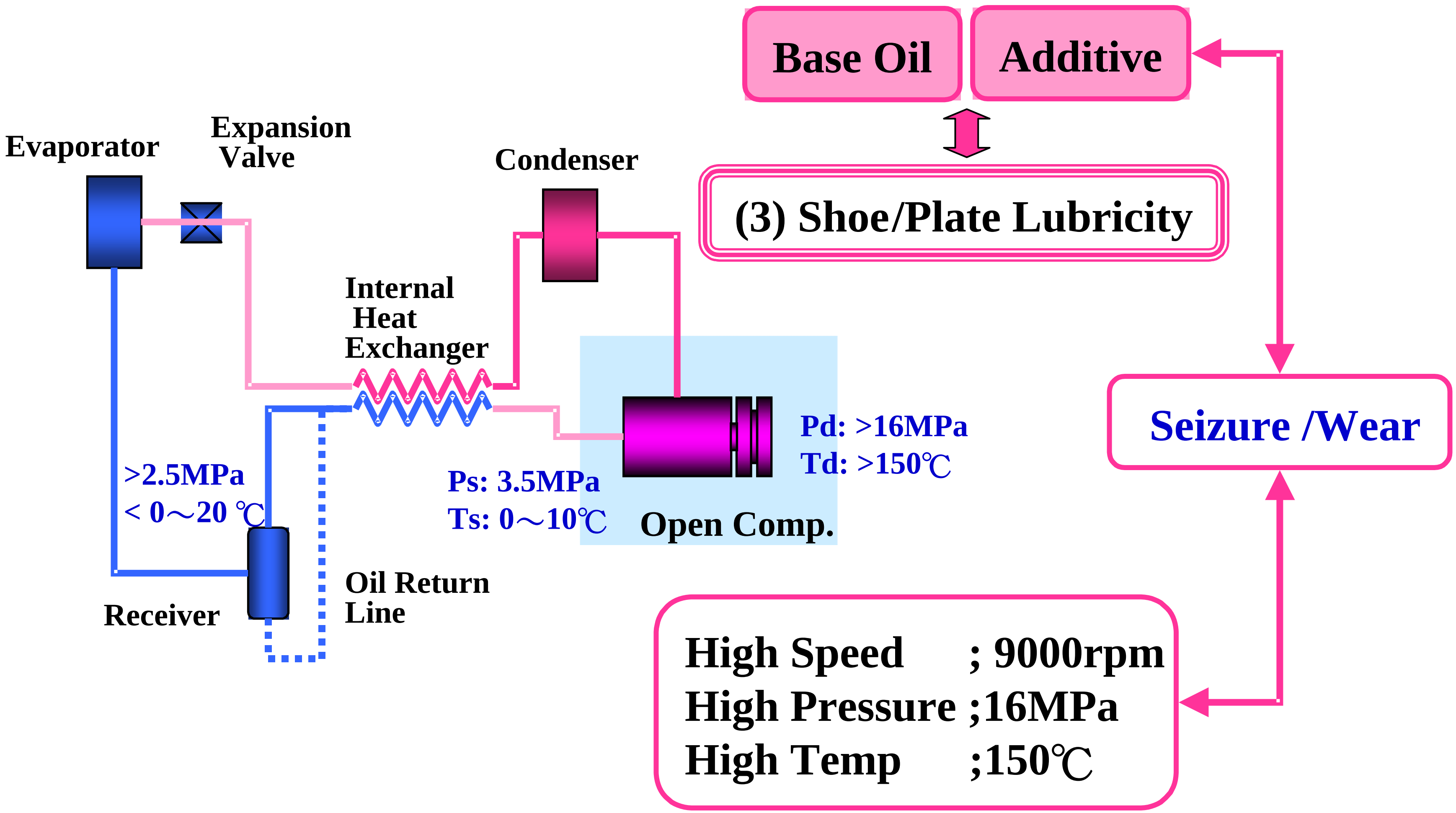
Lubricating Area

	100℃, 14MPa	
	Oil/CO2 (%)	Mixture Viscosity (mm^2/s)
PAG#9	83/17	3.3
PAG#20	83/17	6.4
POE#17	80/20	2.8

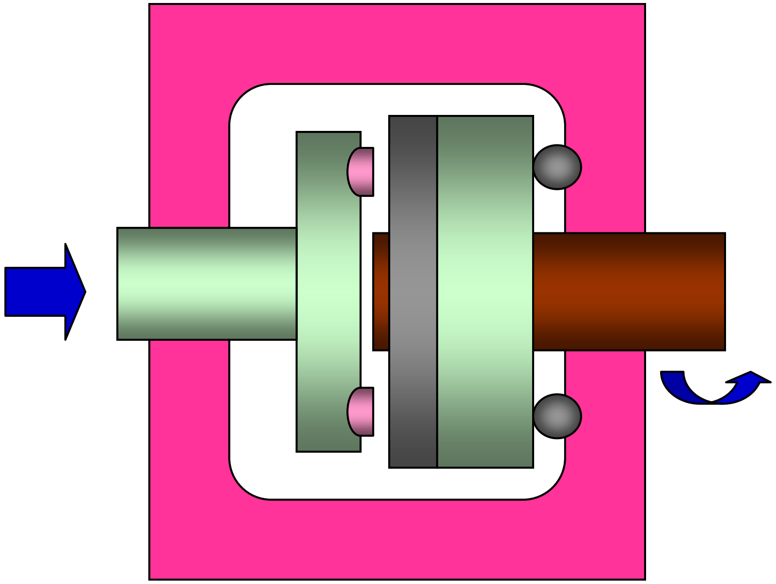
PAG

Good Lubricity

(3) Shoe/Plate Lubricity



Shoe/Plate Friction Test

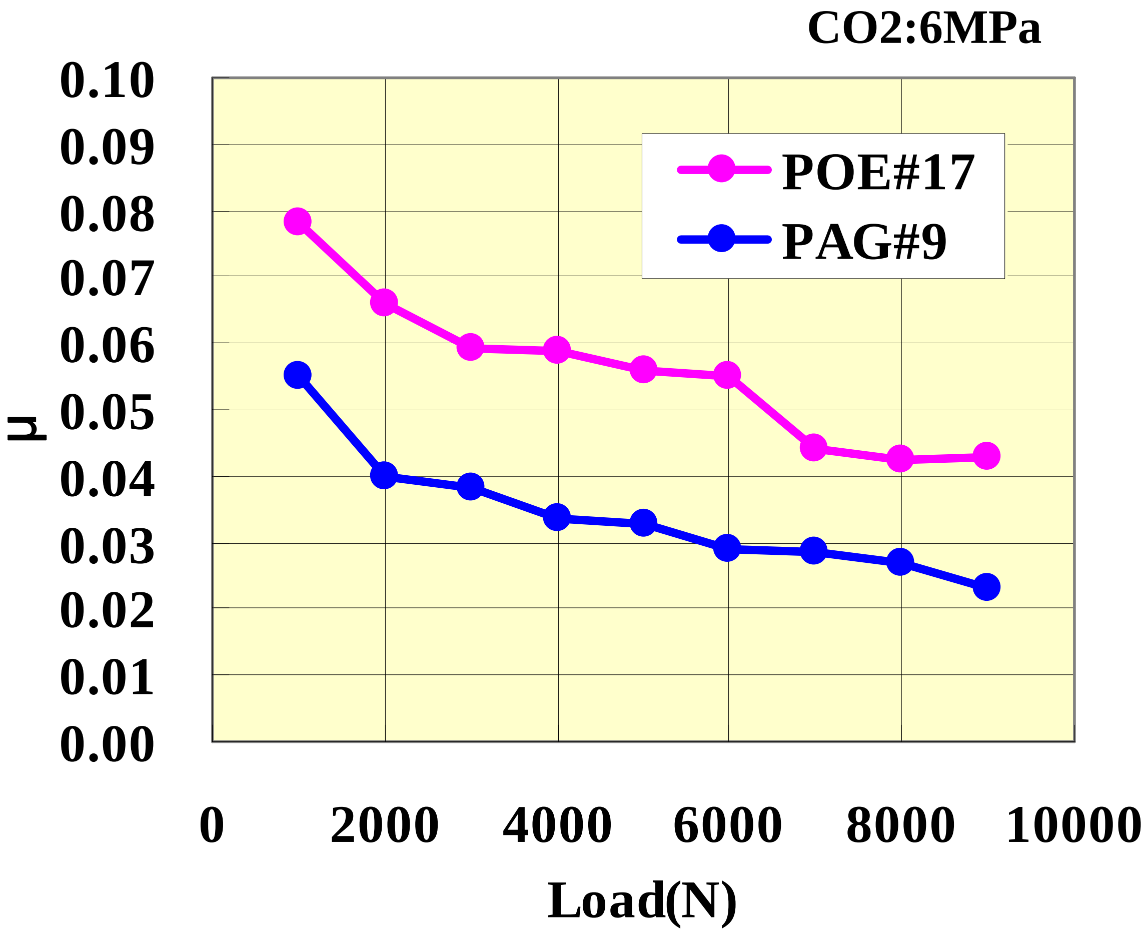


Shoe/Plate Wear Tester

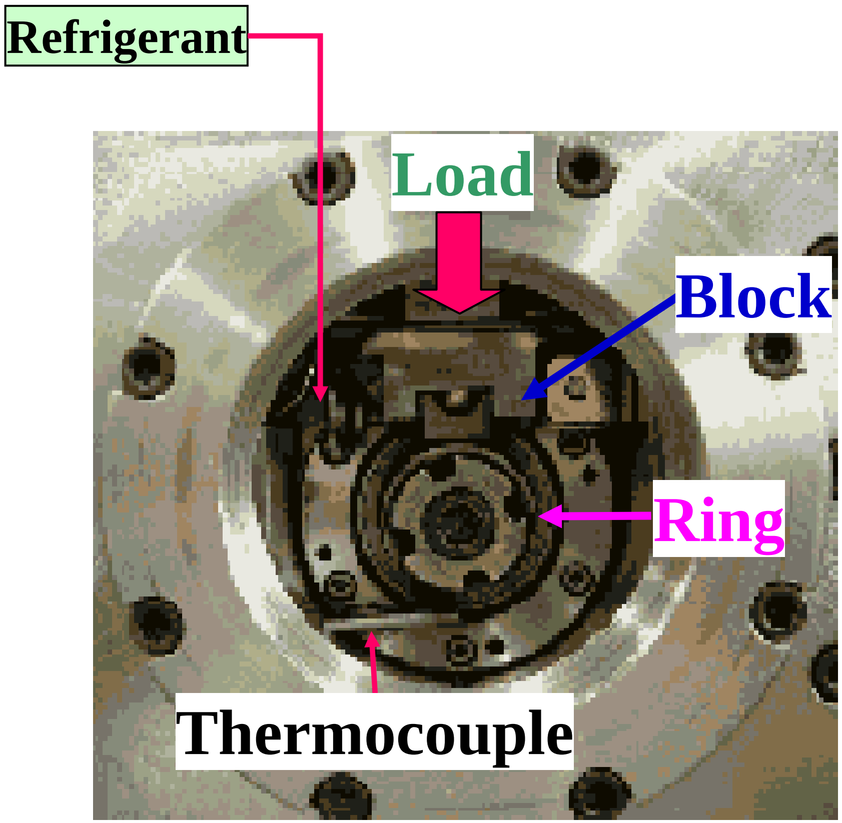
Test Condition

		Friction Test
Shoe		FC
Swash Plate		A390
Speed	(m/s)	4
Load(100N Step up)	(N)	100 ~ 9800
Temperature	(℃)	140
Oil	(cc)	200
Pressure of CO_2	(MPa)	6

Friction of PAG and POE



Block on Ring Wear Test

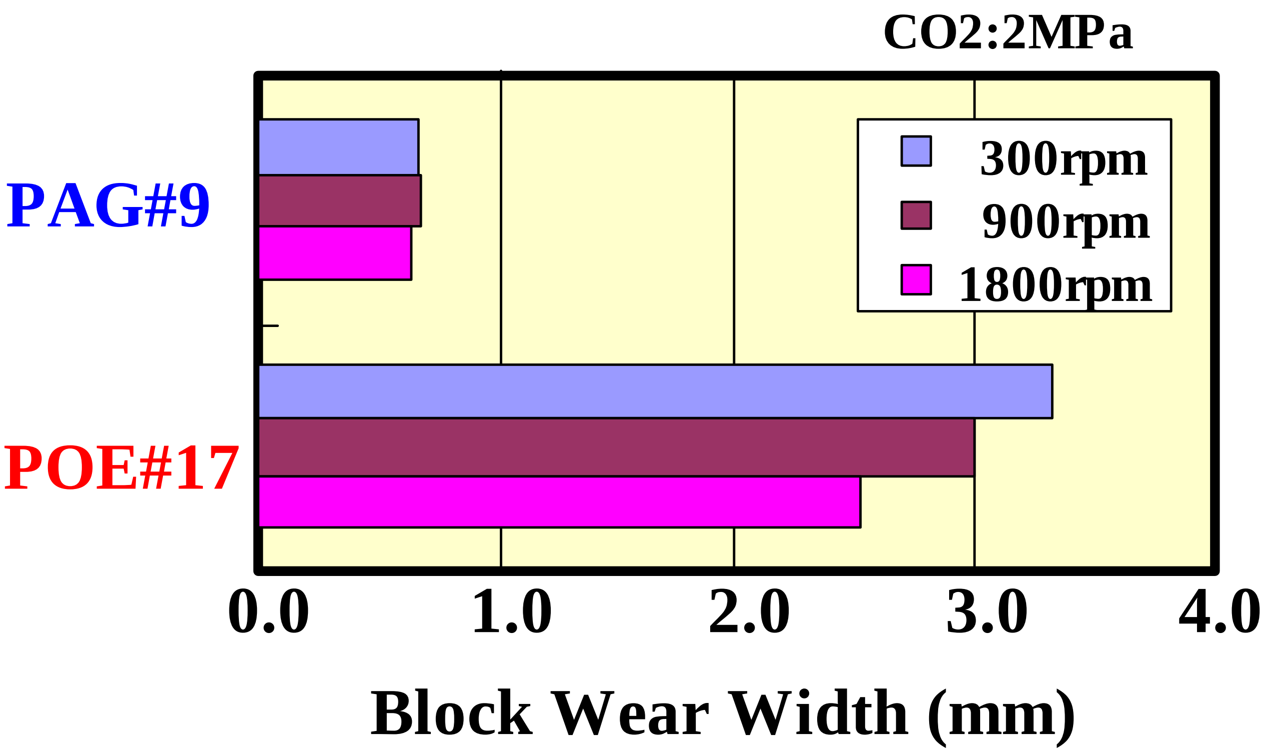


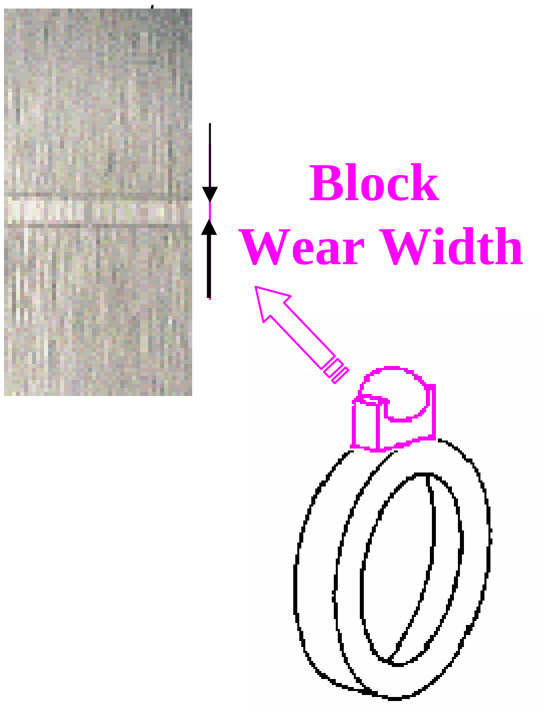
Hermetic Type Block-on-Ring Tester

Test Condition

Block	Al (A4032)		
Ring	Steel(SUJ2)		
Load(N)	1372		
Revolution(rpm)	300	900	1800
Test Time(min)	60		
CO_2 Pressure(MPa)	2		
Oil Temperature(℃)	50		

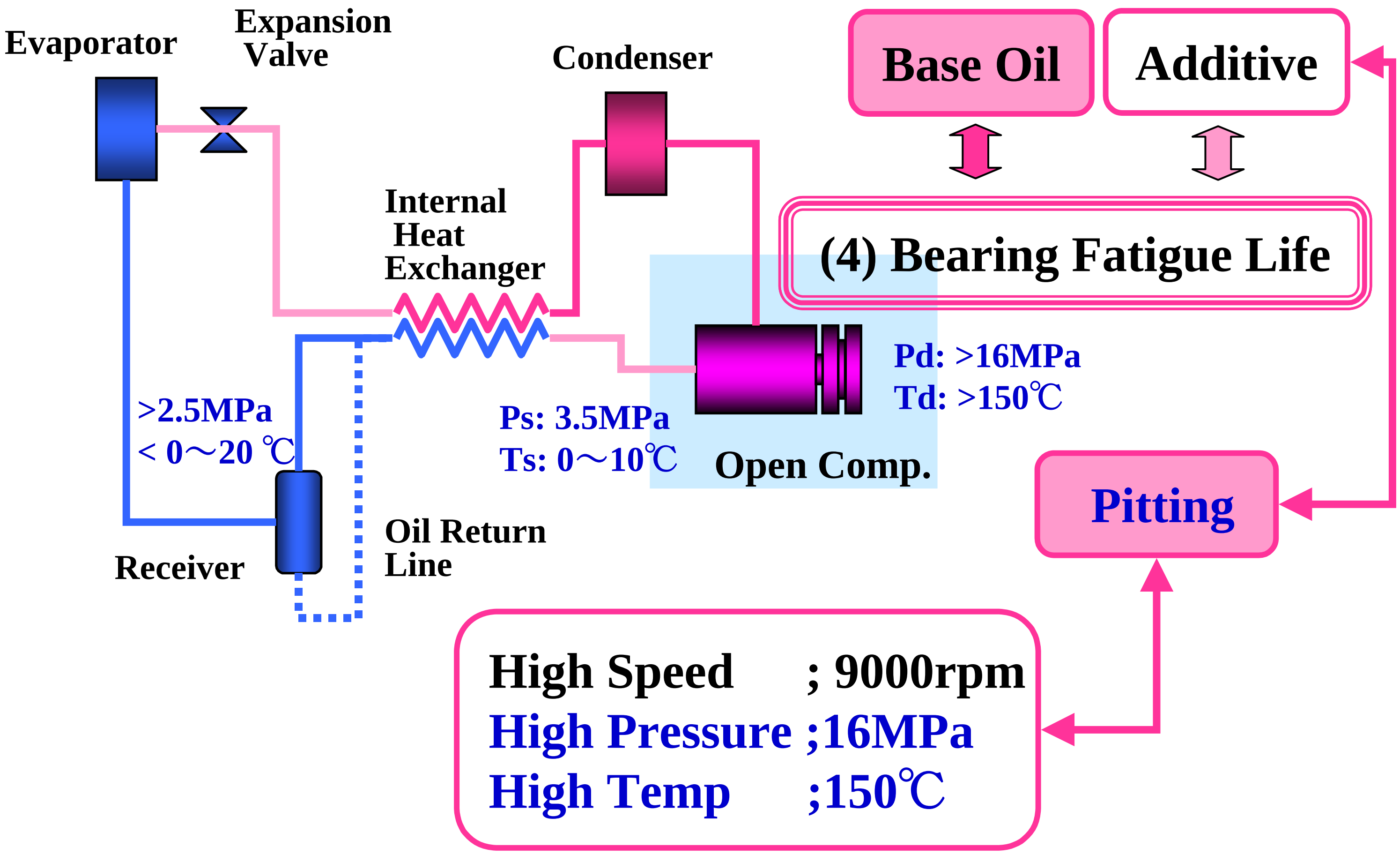
Wear of PAG and POE





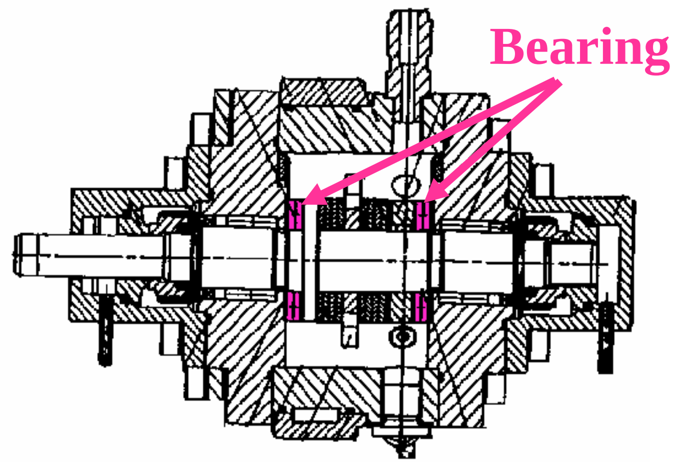
(4) Bearing Fatigue Life

For Design of Bearing with Oil/CO_2 Mixture



Fatigue Life Test Method

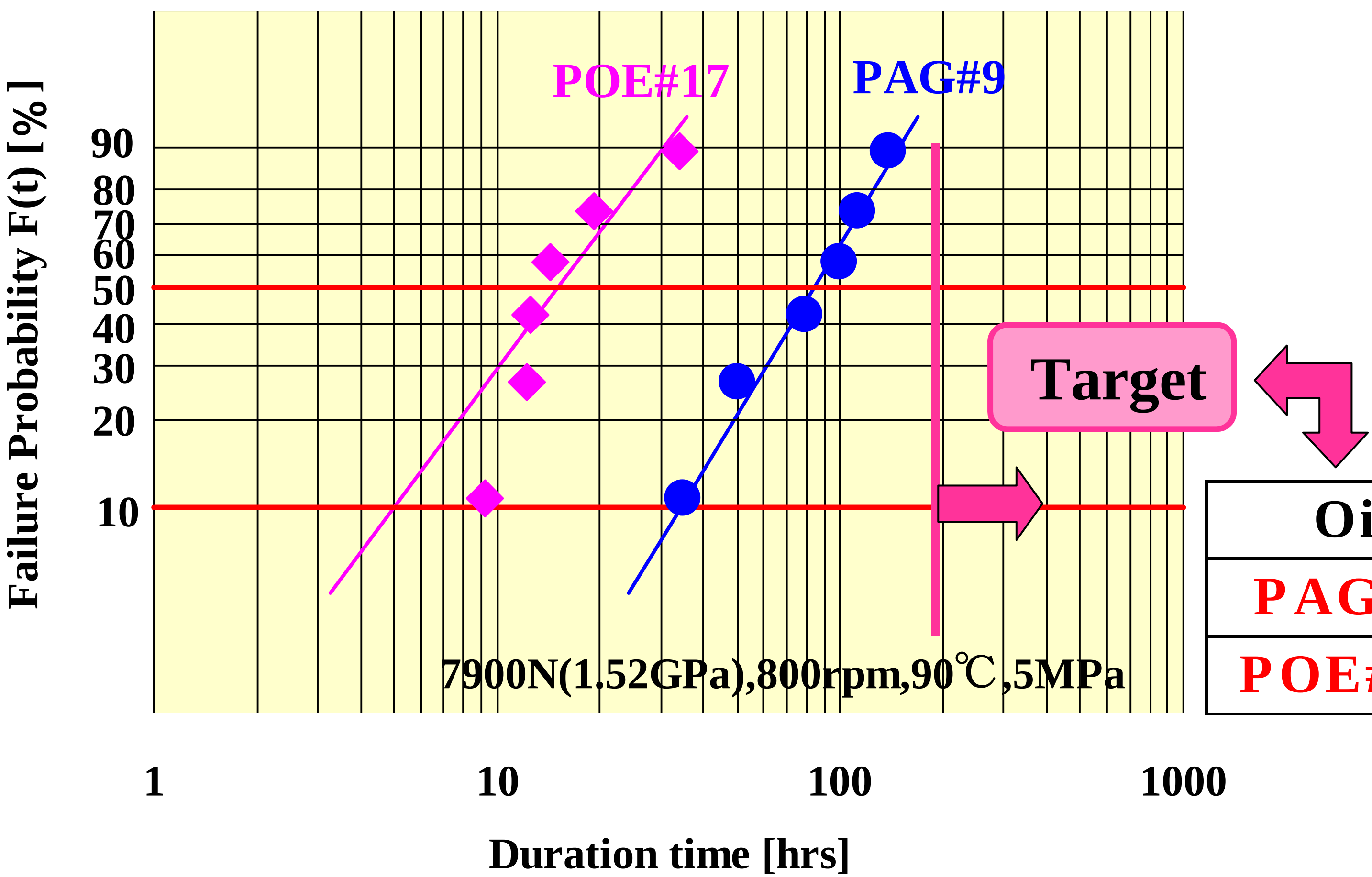
Hermetic Type
Fatigue Life Tester



Test Condition

Needle[4.5φ x5.3mm]		St3(10 Needles)
Disc		Ck67
Speed	(rpm)	800
Axial Load	(N)	7900
Pmax	(GPa)	1.52
Oil Temperatur	(℃)	90
Oil amount	(cc)	50
CO_2-Pressure	(MPa)	5

Fatigue Life of PAG and POE with CO_2

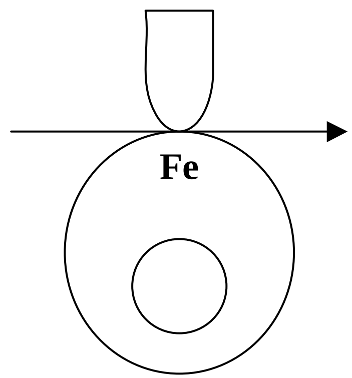


Oil	L10(h)
PAG#9	32.2
POE#17	4.9

Tribochemistry of PAG

PAG#9

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



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

No Reaction

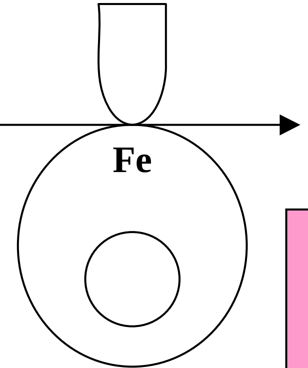
⇩

Good Lubricity

Tribochemistry of POE

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

POE#17



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

Iron Carbonate Soap

↓

Seizure,Wear,Fatigue Life

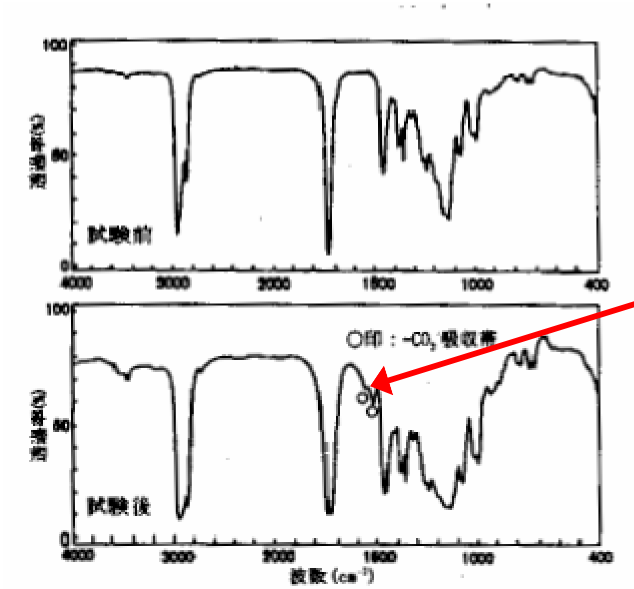


図4. HS-POEのIRチャート

1520, 1560cm^{-1}

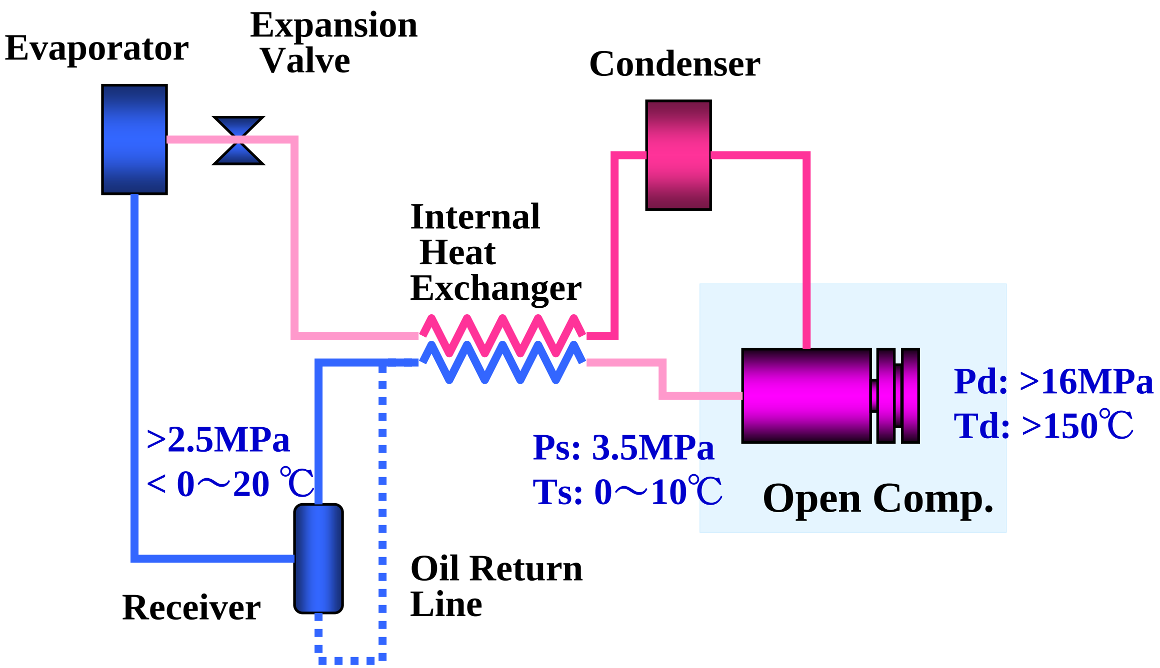
Carbonium ion(-CO^{2-})

C-O Bond Stretching Vibration

(5) Stability

Reaction of Various Material with Oil/CO_2 Mixture

(5) Stability ⟷ **Base Oil** | **Additive**



< Factor >

Heat

Oxygen in Air

Water

< EFFECT >

Thermal Decomposition

Oxidation

Hydrolysis

Thermal ,Oxidation and Hydrolytic Stability

Stability Tests Method

CO_2 Autoclave Test

	Thermal Stability Test	Oxidation Stability Test	Hydrolytic Stability Test
Temperature (℃)		200	
Time (days)		10	
Oil (g)		50	
CO_2 (g)		10	
Air (cc)	-	50	-
H_2O (ppm)	-	-	300
Catalyst		Fe,Cu,Al	

Stability of PAGs and POE with CO_2

(CO_2 Autoclave Test Results)

CO_2 Thermal Stability Test

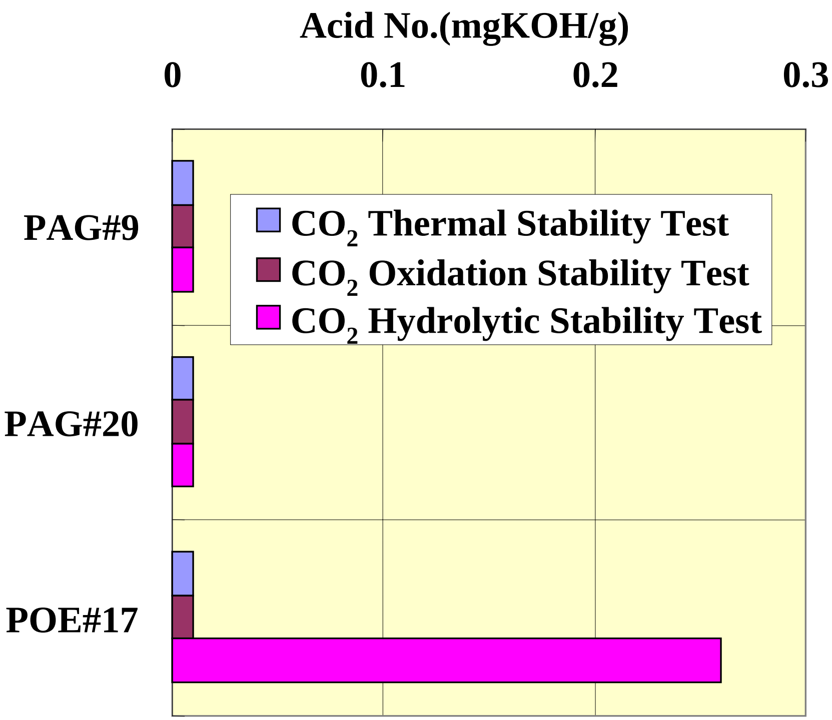
		PAG#9	PAG#20	POE#17
Appearance	Oil	Good	Good	Good
	Cat .	Good	Good	Fe→ black
Acid No.(mgKOH/g)		0.01	0.01	0.01

CO_2 Oxidation Stability Test

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

CO_2 Hydrolytic Stability Test

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



POE

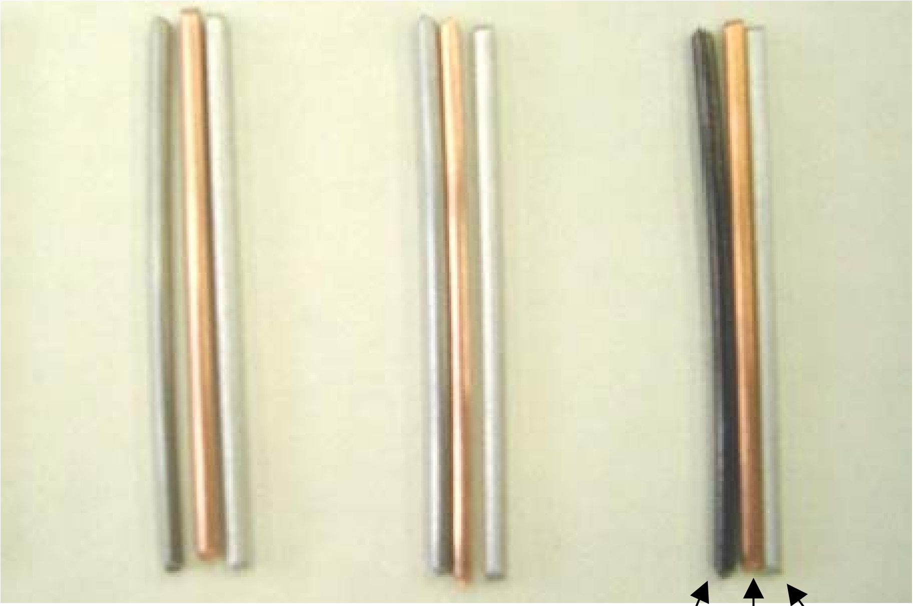
Hydrolysis $RCOOR + H_2O \rightarrow RCOOH + HOR$

Reaction with Iron $RCOOR + Fe \rightarrow Fe$(Black Surface)

Comparison with PAGs and POE of Catalyst in Autoclave Test

CO_2 Thermal Stability Test Result

PAG#9 PAG#20 POE#17



Fe Cu Al

Conclusion

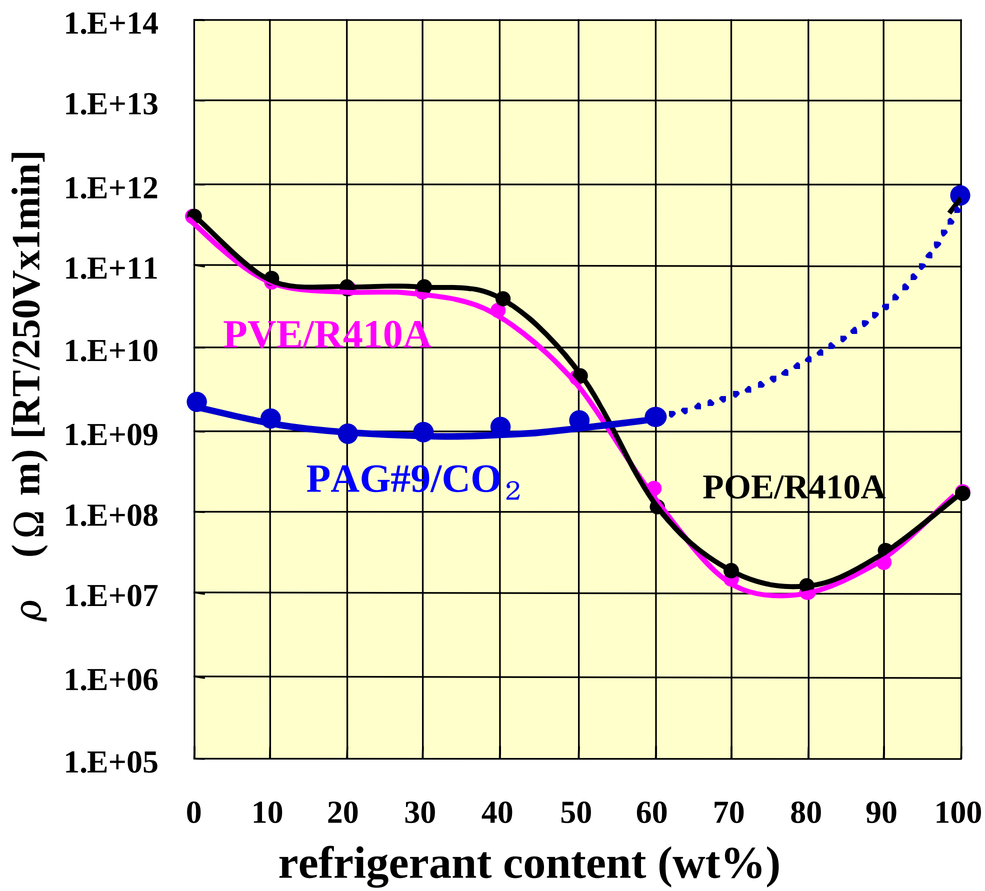
		PAG#9	POE#17
(1)	-40℃ Starting Torque	good	poor
(2)	Oil Return	poor	good
(3)	Shoe/Plate Lubricity	good	poor
(4)	Bearing Fatigue Life	good	poor
(5)	Stability	good	poor

PAG shows good characteristics

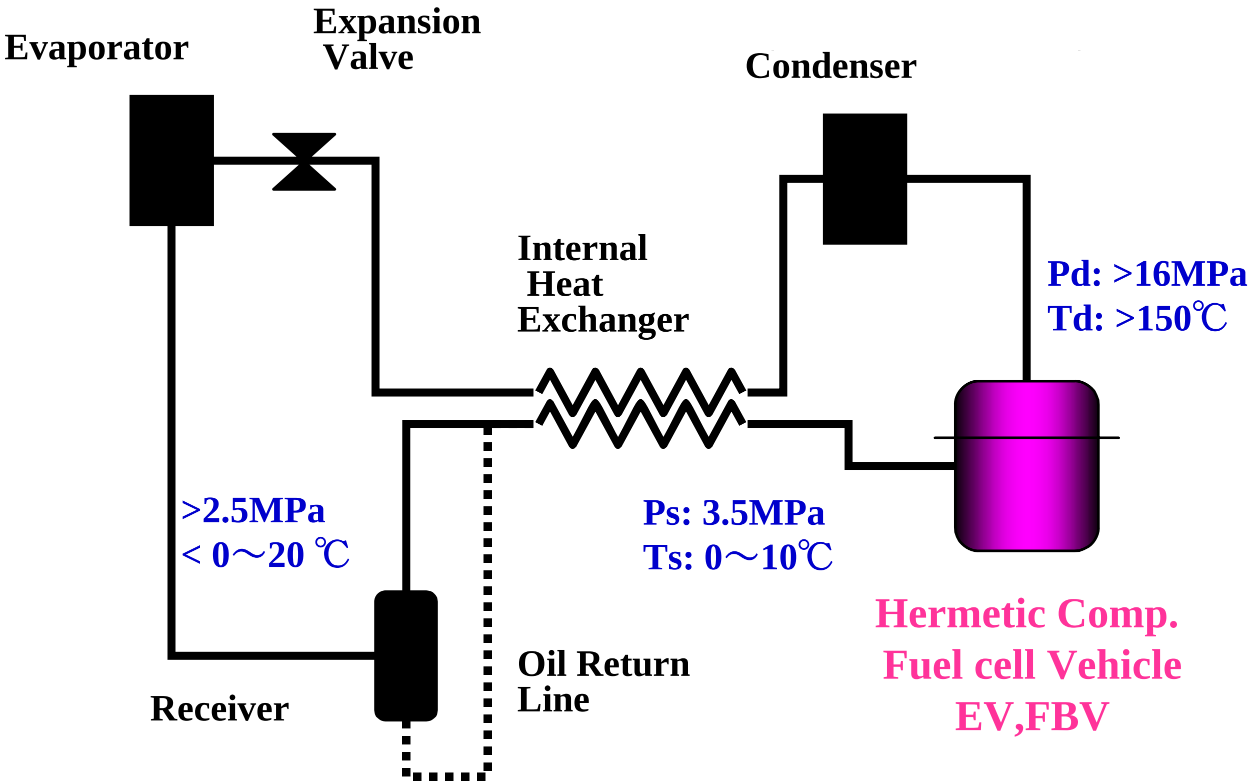
for Automobile A/C with CO_2

Approval of PAG for Hermetic Compressors with CO_2

Volumetric Resistivity of PAG with CO_2



CO_2 A/C System for Fuel cell Vehicle with PAG



Japanese OEM's are choosing PAG#9