Evaluations of PVE Lubricants for Refrigeration and Air Conditioning system with the Low GWP Refrigerants

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Abstract. For the prevention of global warming, various low GWP refrigerants (R1234yf, R1234ze, R448A, R449A, R452A, R452B, R454B etc.) are proposed as the alternative of R410A and R404A for refrigeration and air conditioning system. PVE lubricants were developed for refrigeration and air-conditioning system with low GWP refrigerants. In this report, the combinations of the low GWP refrigerants and lubricant were evaluated. The evaluation items are physical properties (miscibility, solubility, viscosity, and electric insulation), thermal stability and lubricity.

1. Introduction

Now, the HFC refrigerants of the ODP (0) are used for the refrigerating equipment. Since the HFC refrigerants had the high GWP, it was set to one of the greenhouse gas by the Kyoto Protocol in 1997, and became a candidate for reduction. At the F gas regulations of Europe, the refrigerants for refrigerator with hermetic compressor will be upper limit of GWP 2500. And, the refrigerants for RAC will be upper limit of GWP 750. In the industry of refrigeration and air conditioning systems, it has been promoting that the study of low GWP refrigerants. [1] The HFO refrigerants (R1234yf and R1234ze) and the HFO blend refrigerants (R448A, R449A, R452A, R452B, R454B etc.) of the low GWP refrigerants are investigated as one of alternative technology of R404A and R410A. Then, it is necessary to evaluate the specifications and performance of these refrigerants and lubricants.

However, it was checked that the present PVE is inferior in the stability of the HFO refrigerants. So, the development of PVE optimized the new stabilizer for improvement in stability.

In this report, it was evaluated that the relationship between various low GWP refrigerants and PVE lubricants. The evaluation items are physical properties (miscibility, solubility, mixture viscosity and volumetric resistivity) and thermal stability and lubricity.

2. Experimental

2.1. *Lubricants and Refrigerants*

The evaluated lubricants were PVEs. The specifications of PVE are shown table1 in the chemical structure of PVE shown in Figure 1. PVE32A and PVE68A were included the antioxidant, the acid

catcher, and antiwear for R404A and R410A application. The development of PVE32B and PVE68B were added the new stabilizer to PVE32A and PVE68A for HFO application.
Table 2 shows GWP, molecular structure, and refrigerant components of the evaluated refrigerants. The evaluated low GWP refrigerants were seven kinds. Alternative of R404A was considered with R448A, R449A and R452A. Alternative of R410A was considered by R452B and R454B. The evaluation was performed by the method shown in the sub-sections 2.2~2.6 below.

Table 1 Specification of PVEs

Lubricant		PVE32A	PVE32B	PVE68A	PVE68B
Apprication		R404A	HFO	R410A	HFO
Viscosity @40℃ (mm^2/s)		32.40	33.19	66.57	68.41
Viscosity @100℃ (mm^2/s)		5.120	5.260	8.037	8.316
Viscosity Index		78	84	84	88
Density @15℃ (g/cm^3)		0.925	0.936	0.937	0.944
Acid Number (mgKOH/g)		0.01>	0.01>	0.01>	0.01>
additive	antiwear	include	include	include	include
	antioxidant	include	include	include	include
	acid catcher	include	include	include	include
	New stabilizer	-	include	-	include

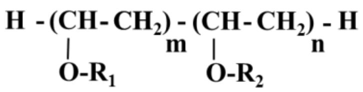


Figure 1 Chemical Structure of PVE

Table 2 Specification of Refrigerants

Refrigerant			R404A	R448A	R449A	R452A	R410A	R452B	R454B	R1234ze	R1234yf
GWP			3920	1273	1397	2140	2090	675	460	6	4
Refrigerant Compoment (wt%)	R32	CH_2F_2		26	24.3	11	50	67	68.9		
	R125	CF_3CHF_2	44	26	24.7	59	50	7			
	R134a	CF_3CH_2F	4	21	25.7						
	R143a	CF_3CH_3	52								
	R1234ze	$CF_3CH{=}CHF$		7						100	
	R1234yf	$CF_3CF{=}CH_2$		20	25.3	30		26	31.1		100

2.2. Stability

Stability of lubricants and refrigerants mixture was evaluated with the autoclave. Table 3 shows the testing conditions. The influence of air and moisture is also examined. The evaluated analysis item was the acid value.

Table 3 Stability test conditions

Conditions	Test 1	Test 2
Temperature (℃)	175	175
Test time (h)	336	336
Oil amount (g)	30	30
Refrigerant amount (g)	30	30
Water content (ppm)	50>	500
Air pressure (kPa)	0.7>	13
Catalysts	Fe / Cu / Al	Fe / Cu / Al

2.3. Miscibility

Figure 2 shows miscibility test apparatus and method. [2] The test tube is made of the sapphire and it was filled up with lubricant/refrigerant mixture. A photo-sensor is set up to detect light through the tube. The bath temperature is gradually increased (or decreased). Initially the lubricant and refrigerant mixture is clear. As the temperature increased (or decreased), the mixture becomes cloudy appearance which indicate lubricant/refrigerant separation. The two-phase separation temperature of that mixture is determined by the light transmittance of the photo-sensor. The temperature representing the center of this curve is the critical separation temperature (CST). The mixed quantity of lubricant was measured in the range of 5 – 40 wt%.

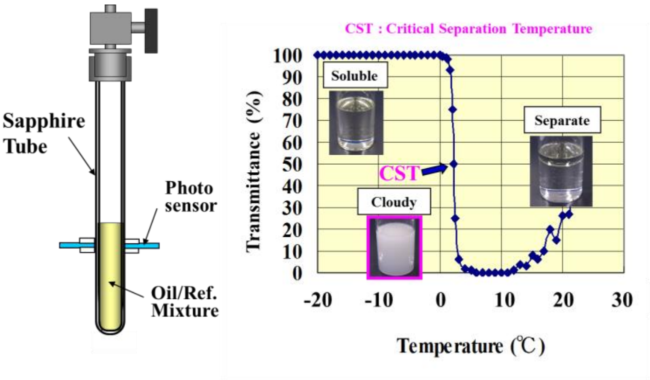


Figure 2 Miscibility test apparatus and method

2.4. Solubility and mixture viscosity

Figure 3 shows the hermetic type viscometer. This apparatus measures both the solubility and mixture viscosity of lubricant/refrigerant mixtures. [3] To measure the viscosity, a capillary-type viscometer in a pressure tight case is used. Solubility was determined by the calculating formula in Figure 3. The Daniel Chart was drawn on measurement data.

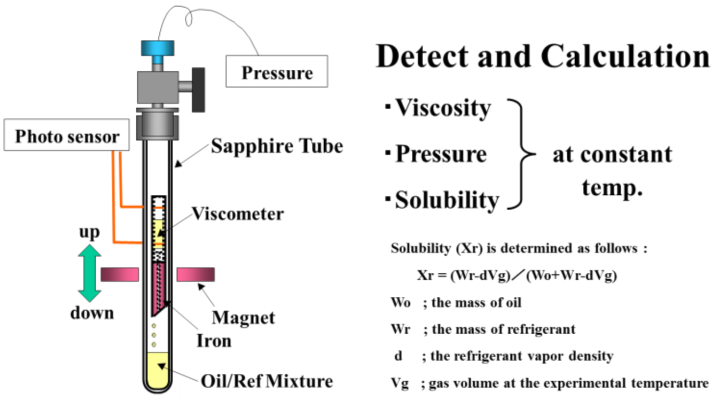


Figure 3 Hermetic type viscometer

2.5. Electric property

Figure 4 shows the hermetic type volumetric resistivity tester. [4] The volumetric resistivity indicates electrical insulation properties of refrigeration lubricant. Volumetric resistivity is a ratio of electrostatic strength to the current density when the direct electric field is impressed to electrode that fills the sample. The volumetric resistivity was measured at varied refrigerant contents (wt%). Test conditions were the voltage (250V) and temperature (20℃).

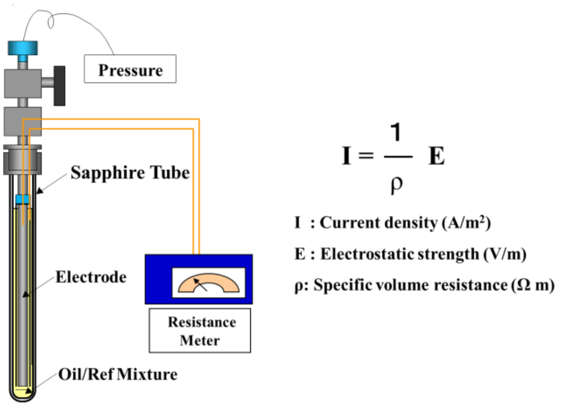
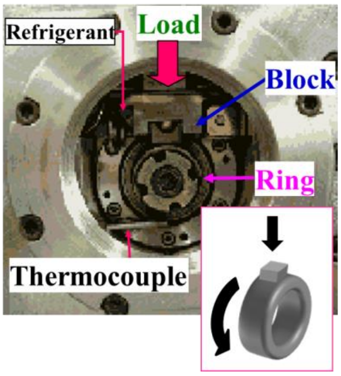


Figure 4 Hermetic type volumetric resistivity tester

2.6. Lubricity

Figure 5 shows the hermetic type Block-on-Ring tester and the lubricating evaluation test conditions. The evaluation was performed by comparison of the wear volume.



Conditions	Test
Ring material	JIS FC250
Block material	JIS SKH51
Temperature (℃)	50
Test time (min)	60
Oil amount (g)	100
Refrigerant pressure(MPa)	0.3
Load (N)	1000
Speed (m/s)	0.5

Figure 5 Hermetic type block-on-ring tester and wear test condition

3. Results and discussions

3.1. Stability

Figure 6 shows the autoclave tests of PVEs with refrigerants. The acid number did not increase in PVE32A / R404A and PVE68A / R410A on the both test conditions. On the other hand, the acid number increased in PVE32A and PVE68A with HFO refrigerants on the test2 condition. The acid number was controlled PVE32B and PVE68B included new stabilizer. It was found that stability of PVE32B and PVE68B was similar to PVEs / HFC refrigerants. The sludge by new stabilizer wasn't seen after the test.

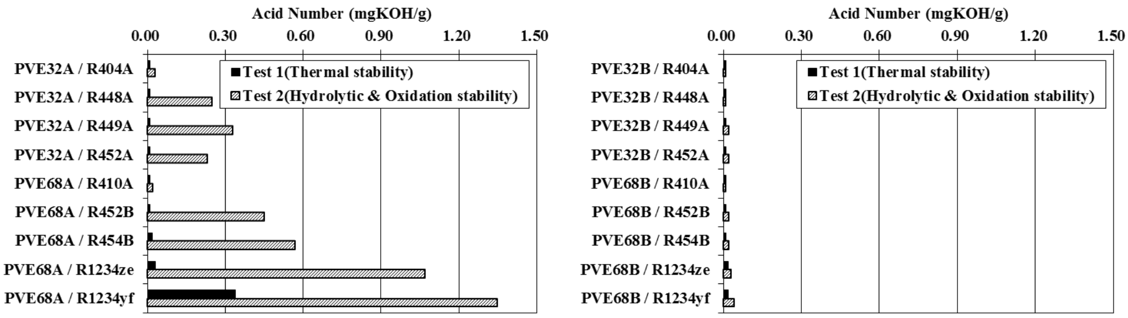


Figure 6 Stability of PVEs with refrigerants

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3.2. Miscibility

Figure 7 shows the miscibility of PVEs with HFC refrigerants (R410A and R404A). At 10wt% of oil content, two-phase separation temperature of PVE32A / R404A and PVE68A / R410A at high temperature were 48℃ and 45℃. Figure 8 shows the miscibility of PVEs with HFO refrigerants (R448A, R449A, R452A, R452B, R454B, R1234ze and R1234yf). HFO refrigerants were more soluble than HFC refrigerants. In particular, the miscibility of PVEs with R1234yf, R1234ze, R448A and R449A were completely soluble within the range of -50℃ to 70℃.

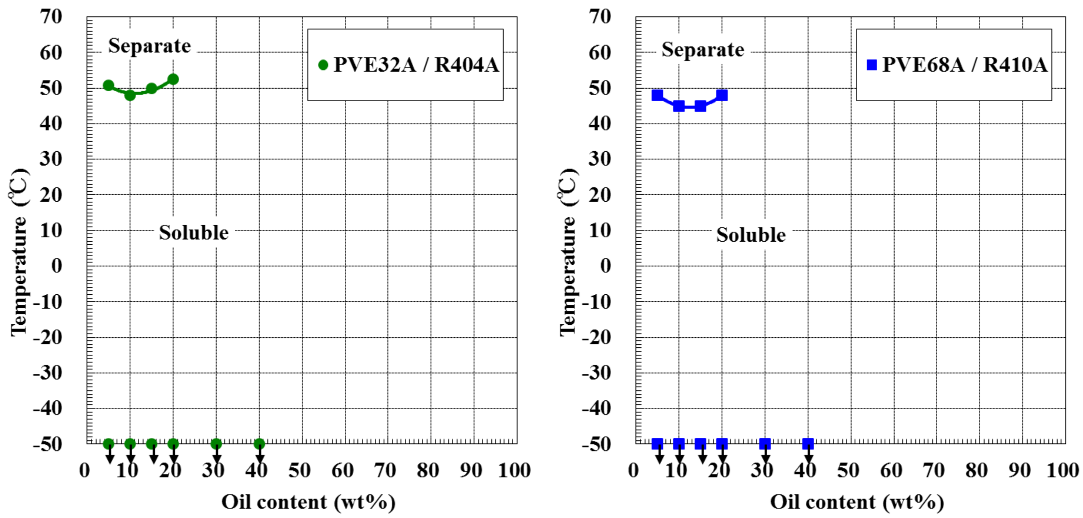

Figure 7 Miscibility of PVEs with HFC refrigerants

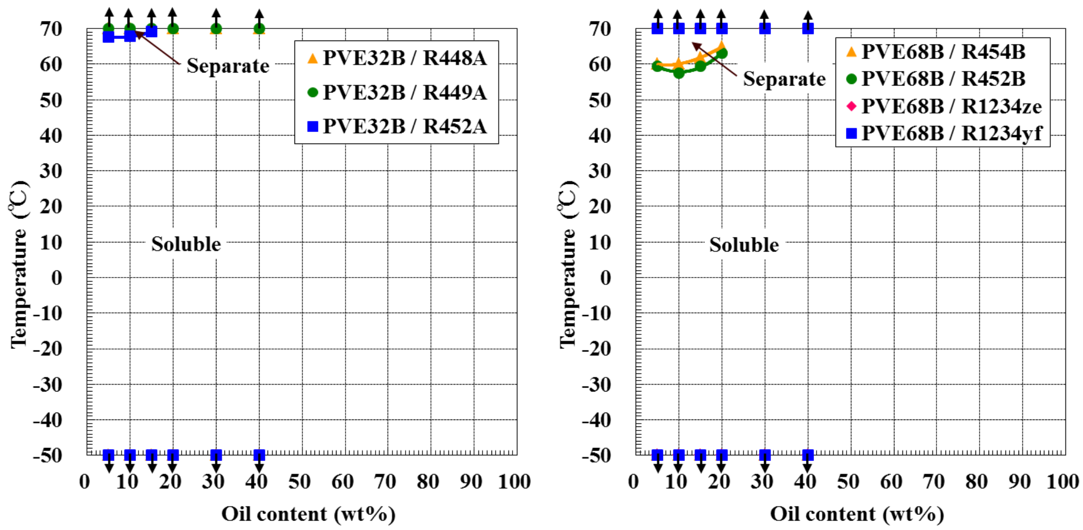

Figure 8 Miscibility of PVEs with HFO refrigerants

3.3. Solubility and mixture viscosity

Figure 9 and 10 show the Daniel Chart of PVEs with refrigerants. As an example, solubility and mixture viscosity of the condition (60℃, 1.5MPa) are shown in table 4.

It was understood that the solubility of PVE32A / R404A was 16%, and that of PVE32B / R1234yf was 50%. So, the solubility of R1234yf was higher than that of R404A. The solubility of PVE32B / R449A and PVE32B / R452A were decreased by PVE32B / R1234yf. On the other hand, the mixture viscosity of R1234yf becomes low for increased solubility.

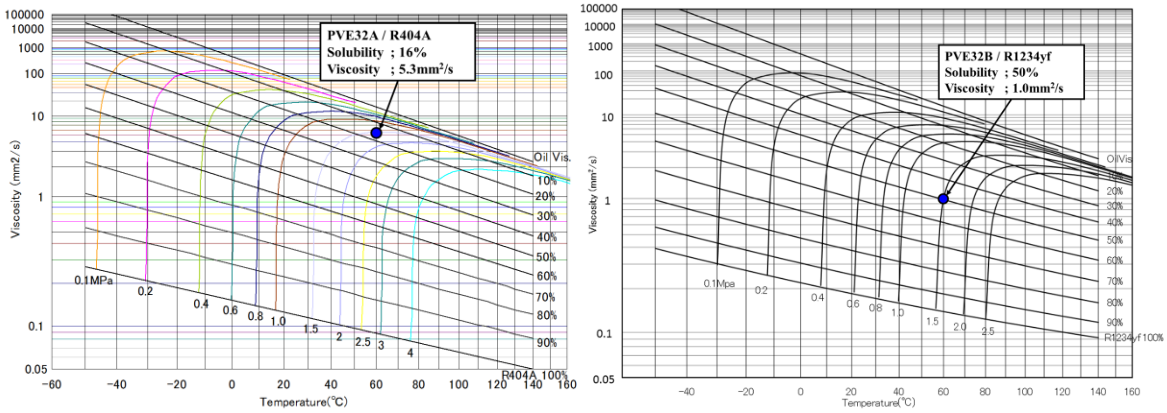

Figure 9 Daniel Chart of PVEs with refrigerants

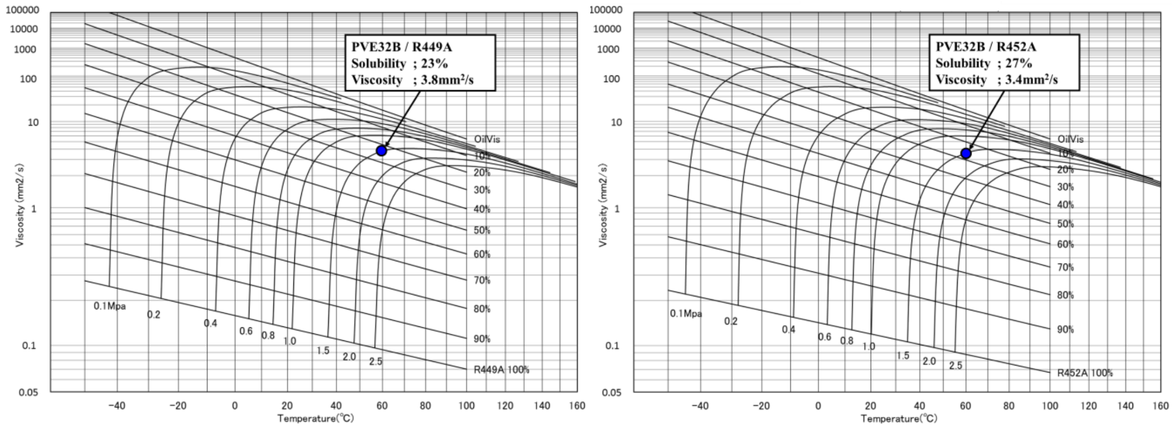

Figure 10 Daniel Chart of PVE32B with refrigerants

Table 4 Solubility and mixture viscosity of PVEs with refrigerants (60℃, 1.5MPa)

Lubricants	Refrigerants	Solubility (wt%)	Viscosity (mm^2/s)
PVE32A	R404A	16	5.3
PVE32B	R449A	23	3.8
PVE32B	R452A	27	3.4
PVE32B	R1234yf	50	1.0

3.4. Electric property

Figure 11 shows the volumetric resistivity of PVEs with refrigerants. The volumetric resistivity of PVE32A and PVE32B were in order of $10^{11}\Omega\cdot m$. It turned out that there is no influence by the new stabilizer. On the other hand, the volumetric resistivity of the refrigerants became high in order of R404A ≈ R449A ≈ R452A < R1234yf. The volumetric resistivity of R449A and R452A didn't increase by R1234yf. The volumetric resistivity of refrigerant mixture decreased with refrigerant content increase. They were slope downward with single logarithmic plot. An order of volumetric resistivity of refrigerants and refrigerant mixture by a constant fraction were the same tendency.

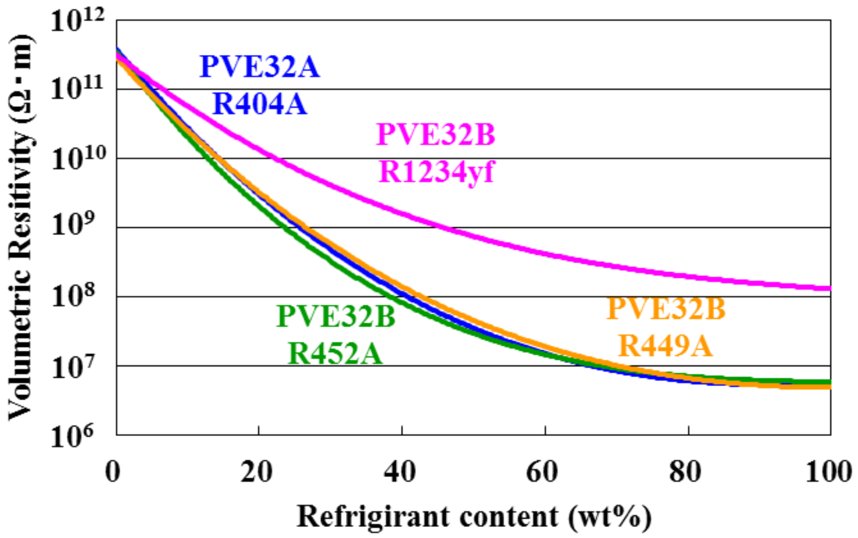

Figure 11 Volumetric resistivity of PVEs with refrigerants

3.5. Lubricity

Table 5 shows lubricity of PVEs with refrigerants. As for PVE32A and PVE32B, PVE68A, PVE68B, there is little wear volume and the difference was not seen. There was no influence by the difference in the refrigerant, and lubricity was good under the examination conditions.

Table 5 Lubricity of PVEs with refrigerants

Lubricants	Refrigerants	Ring Wear (mg)	Lubricants	Refrigerants	Ring Wear (mg)
PVE32A	R404A	1.6	PVE68A	R410A	1.2
PVE32B	R448A	1.5	PVE68B	R452B	1.1
PVE32B	R449A	1.5	PVE68B	R454B	1.1
PVE32B	R452A	1.5	PVE68B	R1234ze	0.9
PVE32B	R1234yf	1.3	PVE68B	R1234yf	0.7

4. Conclusions

It was evaluated that the relationship between the low GWP refrigerants and PVE lubricants. The evaluation items are physical properties (miscibility, solubility, mixture viscosity and volumetric resistivity) and thermal stability and lubricity. The development of PVE32B and PVE68B included new stabilizer for improvement in stability with HFO refrigerants (R1234ze and R1234yf). Furthermore, PVE32B and PVE68B can be used also for lubricant with the HFO blend refrigerants (R448A, R449A, R452A, R452B and R454B).

References

[1] H. Hara and M. Oono, I. Iwata. 2010 *International Symposium on Next-generation Air Conditioning and Refrigeration Technology* NS26.
[2] JP2823123
[3] JP3711303
[4] JP5624782