Properties of lubricants for refrigeration system with the low GWP refrigerants

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Properties of lubricants for refrigeration 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.) were proposed as the alternative to HFC refrigerants for refrigeration system. In this report, the combinations of the low GWP refrigerants and lubricants were evaluated. The evaluation items are physical properties (miscibility, solubility, viscosity, and electric property)and thermal stability.

1. INTRODUCTION

For the prevention of global warming, global regulation of HFC refrigerants has begun. At the 28th meeting of the parties to the Montreal Protocol (MOP 28) in 2016, a stepwise reduction based on global warming potential (GWP) of HFC refrigerants was agreed globally. Refrigerants for air-conditioning system and refrigeration system are high GWP, and countermeasures are attracting attention because leakage is large for application and influence on global warming is great.

R410A (GWP = 2090), R404A (GWP = 3920), R134a (GWP = 1430) are currently mainly used as HFC refrigerants for refrigeration system. As regional regulatory trends, F-Gas regulation in Europe requires GWP < 2500 after 2020, the Freon Emission Control Law in Japan requires GWP < 1500 after 2025, SNAP in the United States regulates the refrigerant type to be used sequentially from 2017. The substitution of R404A for refrigerator, which is particularly high in GWP, needs to be promoted. [(1), (2)]

The HFO pure refrigerants (R1234yf) and the HFO blend refrigerants (R448A, R449A etc.) of the low GWP refrigerants are investigated as one of alternative to R404A. Then, it is necessary to evaluate the specifications and performance of these refrigerants and lubricants.

However, it was found that the current PVE is inferior in the stability of the HFO refrigerants. Therefore, in order to improve stability, PVE optimized stabilizer was developed. 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.

2. EXPERIMENTAL

2.1 Lubricants and Refrigerants

The evaluated lubricants were PVEs. The specifications of PVE are shown table 1 in the chemical structure of PVE shown in Figure 1. PVE-A was included the antiwear, the antioxidant and the acid catcher, for R404A application. The development of PVE-B was added the new stabilizer to PVE-A for HFO application.
Table 2 shows GWP, molecular structure, and refrigerant components of the evaluated refrigerants. Three kinds of refrigerants, alternative of R404A, were evaluated. The evaluation was performed by the method shown in the sub-sections 2.2 - 2.5 below.

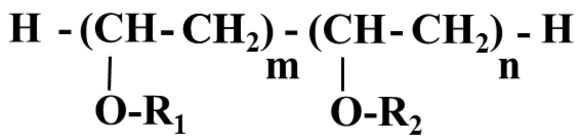


Figure 1: Chemical structure of PVE

Table 1: Specifications of PVE

Lubricants		PVE-A	PVE-B
Application		R404A	HFO
Viscosity@40℃(mm^2/s)		32.40	33.19
Viscosity@100℃(mm^2/s)		5.120	5.260
Viscosity Index		78	84
Density@15℃(g/cm^3)		0.925	0.936
Acid Number(mgKOH/g)		0.01>	0.01>
Additives	Antiwear	Include	Include
	Antioxdant	Include	Include
	Acid catcher	Include	Include
	New stabilizer	-	**Include**

Table 2: Properties of refrigerants

Refrigerants			HFC	HFO blend		HFO
			R404A	R448A	R449A	R1234yf
GWP			3920	1273	1397	4
Refirgerant Compound wt%	R32	CH_2F_2		26	24.3	
	R125	CF_3-CHF_2	44	26	24.7	
	R134a	CF_3-CH_2F	4	21	25.7	
	R143a	CF_3-CH_3	52			
	R1234ze	CF_3-CH=CHF		7		
	R1234yf	CF_3-CF=CH_2		20	25.3	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 content (ppm)	10>	1000
Catalysts	Fe / Cu / Al	Fe / Cu / Al

2.3. Miscibility

Figure 2 shows miscibility test apparatus and method. [3] 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%.

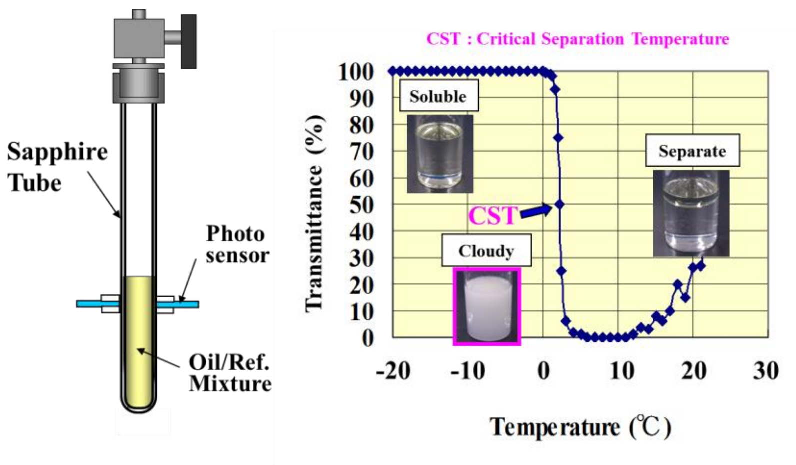


Figure 2: Miscibility test apparatus and method

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. (4) 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.

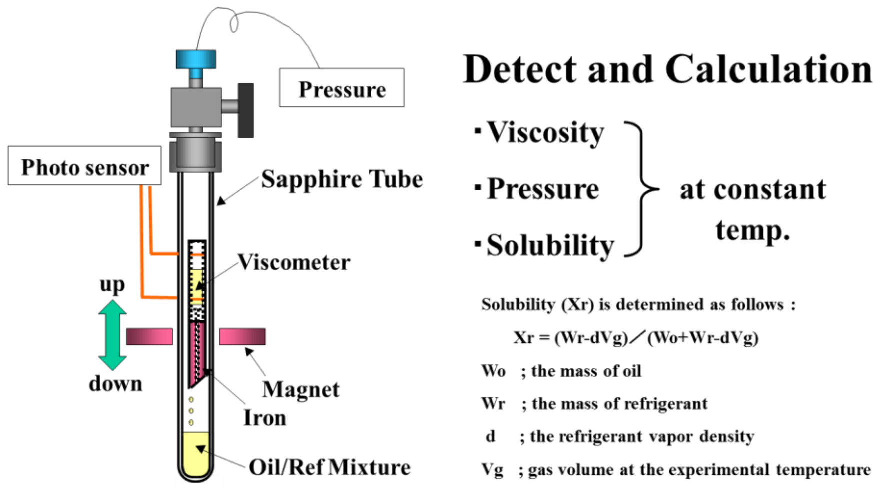


Figure 3: Hermetic type viscometer

2.5 Electric property

Figure 4 shows the hermetic type volumetric resistivity tester. (5) 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℃).

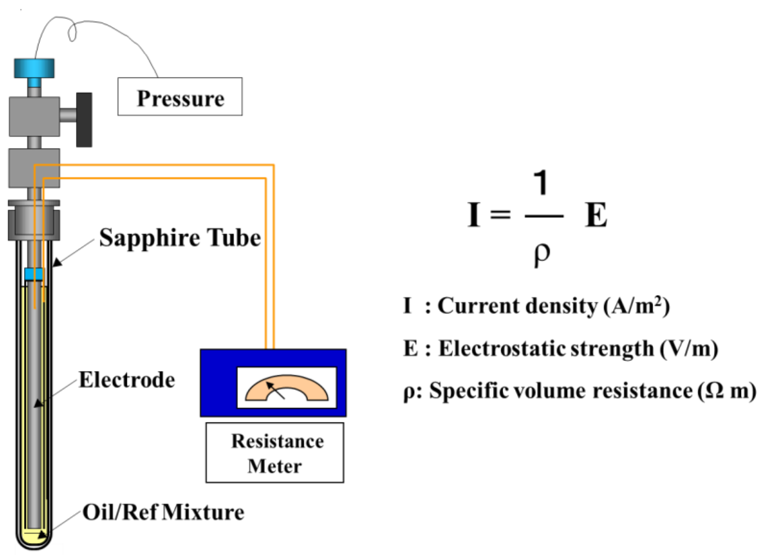


Figure 4: Hermetic type volumetric resistivity tester

3. RESULTS AND DISCUSSIONS

3.1 Stability

Figure 5, 6 shows the autoclave tests of PVEs with refrigerants. The acid number did not increase in PVE-A / R404A on the both test conditions. On the other hand, the acid number increased in PVE-A / HFO refrigerants on the test2 condition. The acid number was controlled PVE-B included new stabilizer. It was found that stability of PVE-B / HFO and HFO blend were similar to PVE-A / R404A.

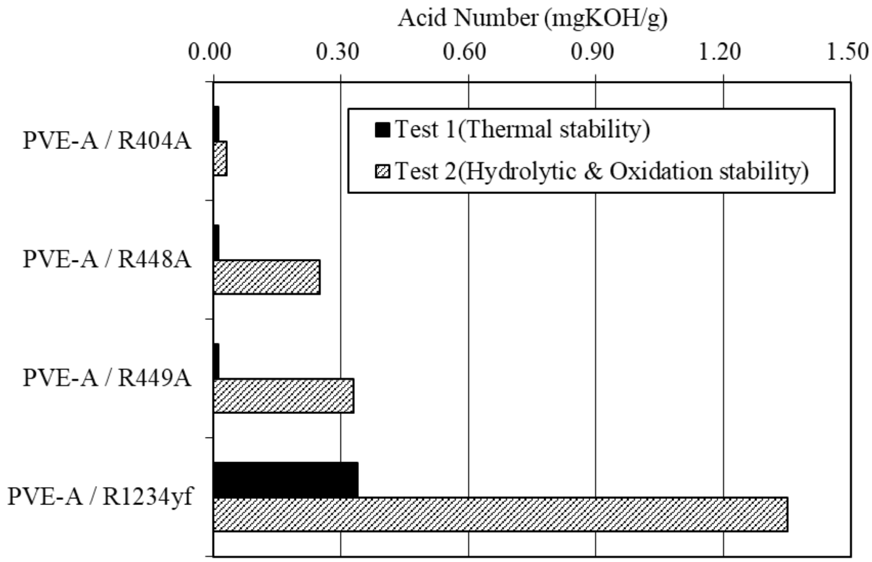


Figure 5: Thermal stability and hydrolytic & oxidation stability of PVE-A/refrigerants

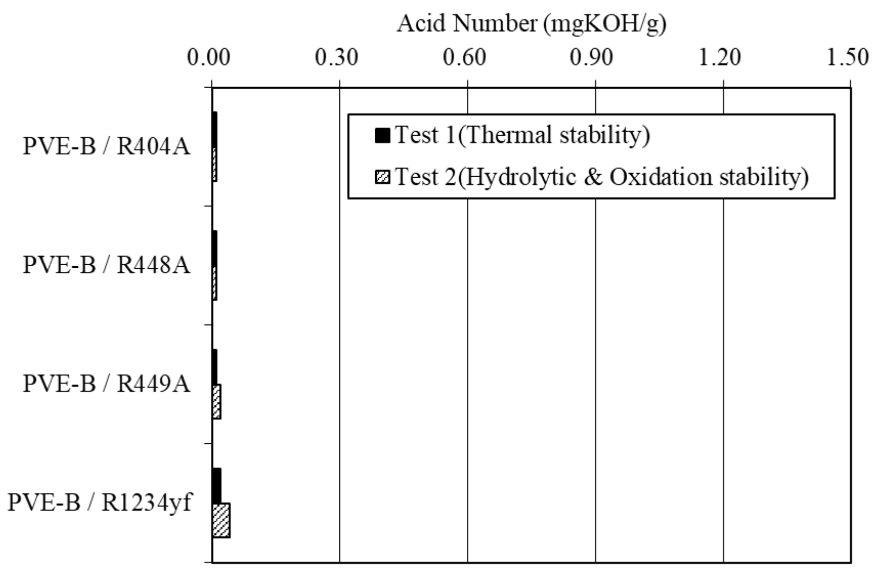
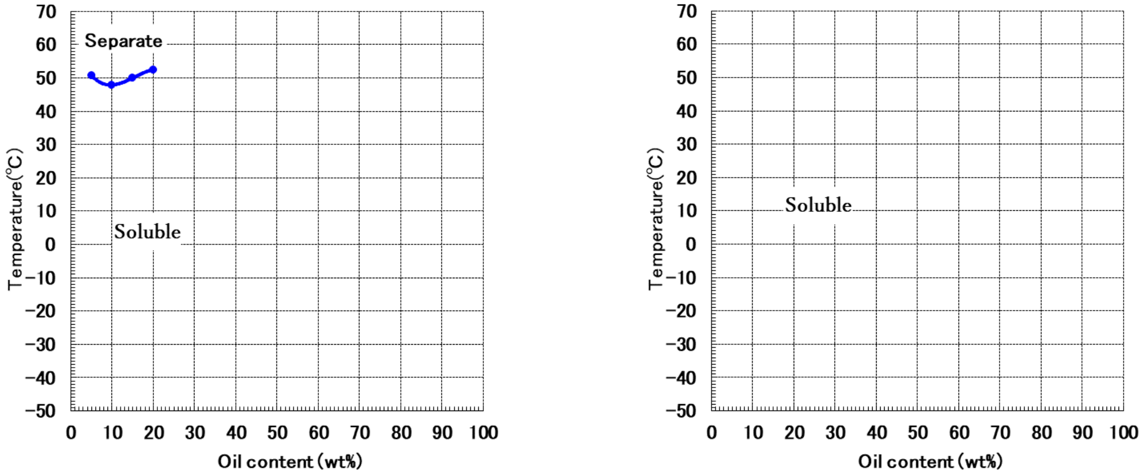


Figure 6: Thermal stability and hydrolytic & oxidation stability of PVE-B/refrigerants

3.2 Miscibility

Figure 7(a) shows the miscibility of PVE-A with HFC refrigerant, R404A. At 10wt% of oil content, two-phase separation temperature of PVE-A / R404A at high temperature was 48℃. Figure 7(b) shows the miscibility of PVE-B with HFO refrigerants (R448A, R449A, and R1234yf). HFO refrigerants were more soluble than HFC refrigerant. The miscibility of PVE-B with R448A, R449A and R1234yf were completely soluble within the range of -50℃ to 70℃.



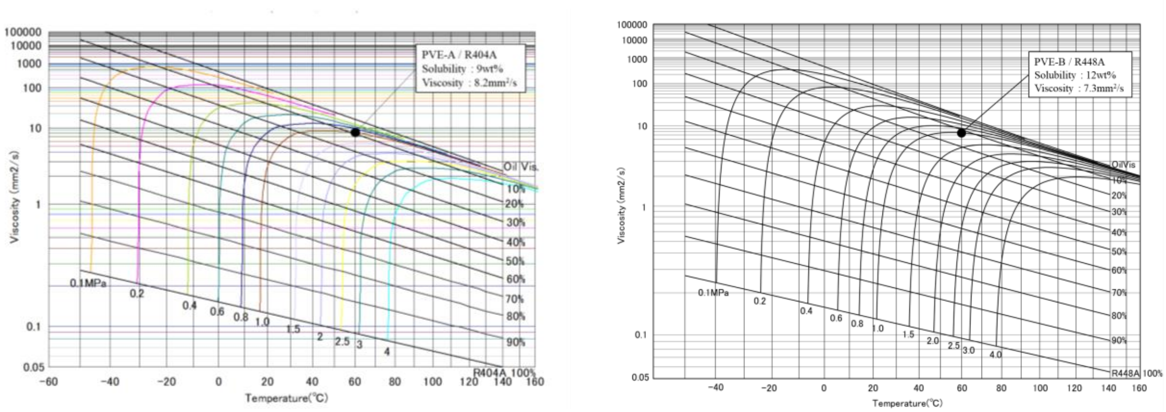
(a) PVE-A with R404A

(b) PVE-B with R448A, R449A, R1234yf

Figure 7: Miscibility of PVEs with refrigerants

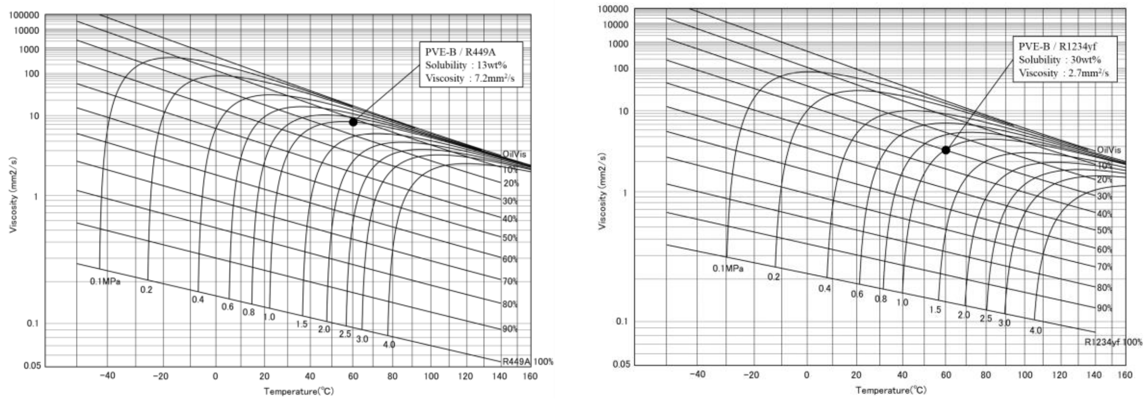
3.3 Solubility and mixture viscosity

Figure 8(a, b, c, d) are the Daniel Chart of PVEs with refrigerants. As an example, solubility and mixture viscosity of the condition (60℃, 1.0MPa) are shown in Table 4. It was understood that the solubility of PVE-A / R404A was 9%, and that of PVE-B / R1234yf was 30%. The solubility of R1234yf was higher than that of R404A. The solubility of PVE-B / R448A and PVE-B / R449A were decreased by including R1234yf.



(a) PVE-A/R404A

(b) PVE-B/R448A



(c) PVE-B/R449A (d) PVE-B/R1234yf

Figure 8: Daniel chart of PVEs with refrigerants

Table 4: Solubility and mixture viscosity of PVEs with refrigerants (60℃, 1.0MPa)

Lubricants	Refrigerants	Solubility (wt%)	Viscosity (mm^2/s)
PVE-A	R404A	9	8.2
PVE-B	R448A	12	7.3
PVE-B	R449A	13	7.2
PVE-B	R1234yf	30	2.7

3.4 Electric property

Figure 9 shows the volumetric resistivity of PVEs with refrigerants. The volumetric resistivity of PVE-A and PVE-B 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 ≈ R448A < R1234yf. The volumetric resistivity of R449A and R448A did not increase by including R1234yf. The volumetric resistivity of refrigerant mixture decreased with refrigerant content increase. They were slope downward with single logarithmic plot. The order of volumetric resistivity of refrigerants and refrigerant mixture by a constant fraction were the same tendency.

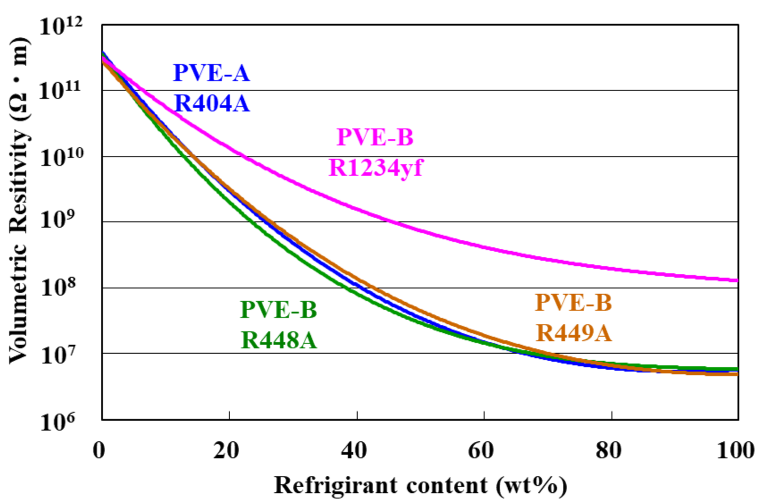


Figure 9: Volumetric resistivity of PVEs with refrigerants

4. CONCLUSIONS

It was evaluated that the relationship between the HFC and HFO blend refrigerants with PVE lubricants. The evaluation items are physical properties (miscibility, solubility, mixture viscosity and volumetric resistivity) and thermal stability. The developed PVE-B contained a new stabilizer and it was able to improve the stability under HFO refrigerants (R1234yf). Furthermore, PVE-B can be used also for lubricant with the HFO blend refrigerants (R448A, R449A).

NOMENCLATURE

GWP	global warming potential
HFC	hydrofluorocarbons
HFO	hydrofluoroolefins
PVE	polyvinyl ether
CST	critical separation temperature

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(3) Patent JP2823123

(4) Patent JP3711303

(5) Patent JP5624782