

## Evaluation of Refrigeration Lubricants for Low GWP refrigerants

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### ABSTRACT

Hydrofluorocarbon (HFC) refrigerants have been replaced by various low global warming potential (GWP) refrigerants in refrigeration systems due to the regulations on greenhouse gas emissions, such as the 2016 Kigali Amendment to the Montreal Protocol. Whereas next-generation hydrofluoroolefin (HFO) refrigerants like R448A and R454C have relatively low GWP, they exhibit lower thermal stability compared to traditional HFC refrigerants. This issue poses a challenge for drop-in replacement in HFC systems with HFO refrigerants, impacting the thermal stability of refrigeration lubricants. In this report, we have conducted thermal stability evaluations of refrigeration lubricants intended for drop-in systems transitioning from HFC refrigerants to HFO refrigerants. In HFO refrigerants, the appropriate stabilizer has reduced the increasing acid number of refrigeration oils. We confirmed the critical importance of using appropriate stabilizers in thermal stability tests for drop-in replacements from HFC to HFO refrigerants.

### 1. INTRODUCTION

A global agreement was reached at the 28th Meeting of the Parties to the Montreal Protocol (MOP28) in 2016 to phase down HFC refrigerants based on their Global Warming Potential (GWP), as part of efforts to prevent global warming. Although the automotive industry has shifted towards refrigerants with very low GWP, air conditioning and low-temperature refrigeration applications continue to use refrigerants with relatively high GWP. Since these sectors use large amounts of refrigerants and leakage significantly impacts global warming, reducing the GWP of refrigerants is an extremely effective measure against climate change.

While R404A is an HFC refrigerant widely used in low-temperature refrigeration systems worldwide, it presents a significant environmental concern due to its high GWP of 3920. Regarding regional regulatory trends, the European F-Gas Regulation mandates GWP values below 2,500 after 2020, Japan's Fluorocarbons Emission Control Law requires GWP values below 1,500 from 2025, and the US SNAP program has been progressively regulating the use of refrigerants since 2017 (Amrane, 2016a and Shibamura, 2016b). In order to comply with these regulations, the transition to HFO refrigerants has already begun in various regions. Next-generation mixed HFO refrigerants including R448A and R454C are promising candidates for achieving these objectives, with GWPs of 1273 and 148, respectively. However, HFO refrigerants are generally known to have lower thermochemical stability than HFC refrigerants. Due to the low thermochemical stability of HFO refrigerants, the refrigerant and its decomposition products can react with the refrigeration oil used to protect the compressor, potentially leading to reduced system efficiency and increased risk of failure. For these reasons, enhancing the thermochemical stability of HFO refrigerants and refrigeration oils is crucial for the effective utilization of HFO refrigerants. Previously, we reported that the addition of appropriate stabilizers to refrigeration lubricants based on polyvinylether (PVE) enhances the

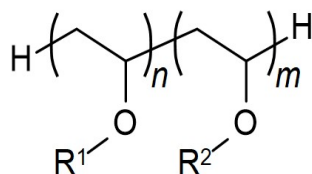
thermochemical stability of the oils under HFO refrigerant conditions (Takagishi, 2021). Therefore, to maximize the utilization of HFO refrigerants, it is essential to pair them with refrigeration oils that are specifically formulated for HFO applications.

Systems employing HFO refrigerants are already in use and are expected to become even more widespread in the future. In this context, it is anticipated that existing HFC refrigerant systems will switch to HFO refrigerants through a drop-in approach. During this process, there is a concern about the impact on thermal stability as small amounts of degraded refrigeration oil may mix into the system filled with HFO refrigerants. This study examines the impact of residual refrigeration oil on the thermal stability of systems that have transitioned from HFC to HFO refrigerants through a drop-in approach.

## 2. EXPERIMENTAL

### 2.1 Lubricants and Refrigerants

In this study, polyvinyl ether (PVE) was used as base oil of refrigeration oil. Figure 1 shows the chemical structure of PVE, where  $R^1$  and  $R^2$  in the figure correspond to alkyl groups. Two types of refrigerant oils, PVE-A and PVE-B, with different additive formulations were prepared and used for testing. PVE-A, which is designed for HFC refrigerants, contains an antioxidant, an anti-wear agent, and an acid catcher, as shown in Table 1. PVE-B, formulated for HFO refrigerants, includes a stabilizer in addition to the additives contained in PVE-A. The basic properties, such as kinematic viscosity, of these PVE samples are similar, as shown in Table 1. In this study, R404A was used as the HFC refrigerant, while R448A and R454C were used as HFO refrigerants. Table 2 summarizes the GWP and components of each refrigerant.



**Figure 1:** Chemical structure of polyvinylether (PVE).  $R^1$  and  $R^2$  correspond to alkyl groups.

**Table 1:** Formulation and properties of refrigeration oil

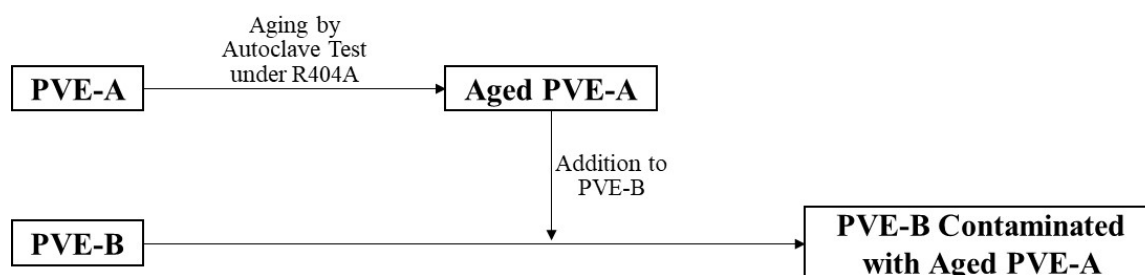
Sample		PVE-A	PVE-B
Application		For HFC	For HFO
Formulation of refrigeration oil	Base oil	PVE	PVE
	Antioxidant	include	include
	Anti-wear agent	include	include
	Acid catcher	include	include
	Stabilizer	-	include
Properties of refrigeration oil	Kinematic viscosity at 40°C (mm <sup>2</sup> /s)	32.40	33.06
	Kinematic viscosity at 100°C (mm <sup>2</sup> /s)	5.120	5.252
	Viscosity index (-)	78	85
	Density, 15°C (g/cm <sup>3</sup> )	0.925	0.927
	Acid number (mgKOH/g)	0.01>	0.01>

### 2.2 Preparation of Samples Contaminated with Aged Oil

Figure 2 shows the sample preparations in this study. PVE-A was aged using autoclave test under condition including 500 ppm of water and 1000 ppm of air in an R404A atmosphere. A small amount of aged PVE-A was added to PVE-B to create contaminated samples. These samples were then used in miscibility and thermal stability tests to evaluate the drop-in approach from HFC to HFO refrigerants.

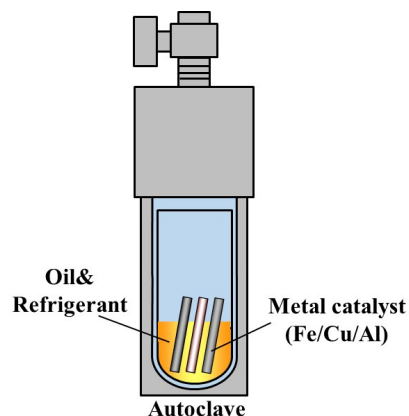
**Table 2:** Component ratio of the mixed refrigerants

Refrigerant used in this work			R404A	R448A	R454C
			HFC	HFO blend	HFO blend
GWP			3,920	1,273	148
Component ratio wt%	R143a	$\text{CF}_3\text{-CH}_3$	52		
	R125	$\text{CF}_3\text{-CHF}_2$	44	26	
	R134a	$\text{CF}_3\text{-CH}_2\text{F}$	4	21	
	R32	$\text{CH}_2\text{F}_2$		26	21.5
	R1234ze(E)	$\text{CF}_3\text{-CH=CHF}$		7	
	R1234yf	$\text{CF}_3\text{-CF=CH}_2$		20	78.5
	Total		100	100	100

**Figure 2:** Flowchart of sample preparation for PVE-B contaminated with aged PVE-A.**Table 3:** Test conditions of thermal stability test

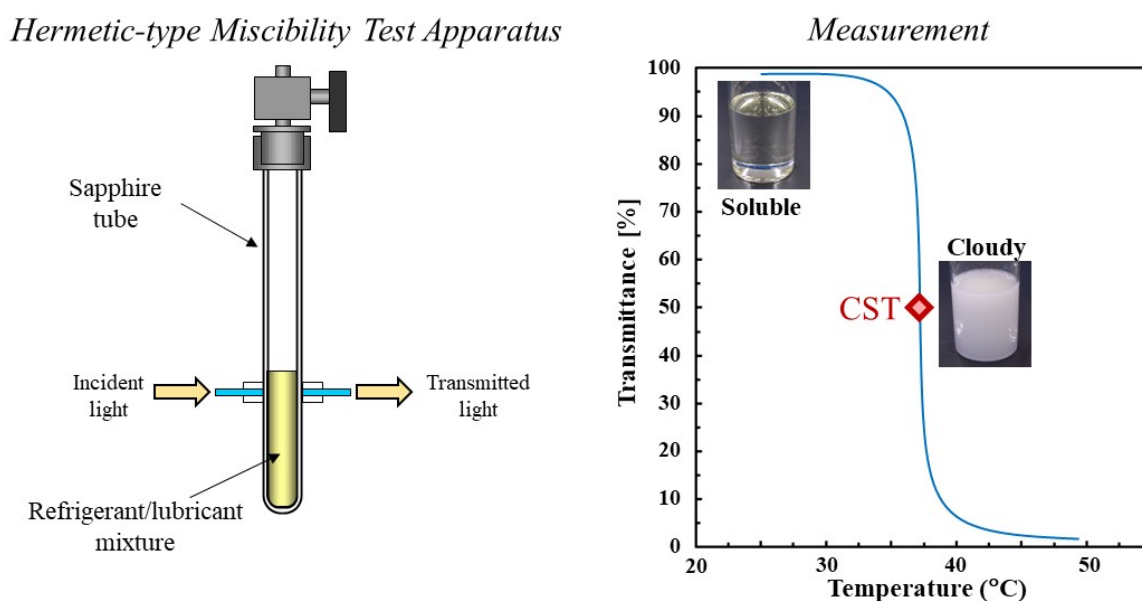
Test conditions	Test 1	Test 2
Temperature (°C)	175	175
Time (h)	336	336
Oil amount (g)	30	30
Refrigerant amount (g)	30	30
Water (ppm) <sup>a</sup>	<50	500
Air (ppm) <sup>b</sup>	<10	1000
Catalyst	Fe/Cu/Al	Fe/Cu/Al

<sup>a</sup>Concentration of water relative to the weight of oil. <sup>b</sup>Concentration of air relative to the weight of refrigerant.

**Figure 3:** Schematic representation of apparatus for thermal stability test using autoclave.

### 2.3 Miscibility Test

The miscibility of refrigeration oil and refrigerant is evaluated by measuring the two-phase separation temperature. Figure 4 illustrates the miscibility test apparatus and method. The test tube, made of sapphire, was filled with oil/refrigerant mixture. Optical transmittance through the tube was monitored as the temperature was progressively increased and decreased. A decrease in optical transmittance, due to clouding, indicated two-phase separation. The midpoint of this transmittance decrease is defined as the critical separation temperature (CST). A phase-separation diagram was generated based on the CSTs at various oil contents.



**Figure 4:** Schematic representation of apparatus and method for measuring two-phase separation temperature. Critical separation temperature (CST) is defined as the midpoint of the decrease in transmittance due to clouding.

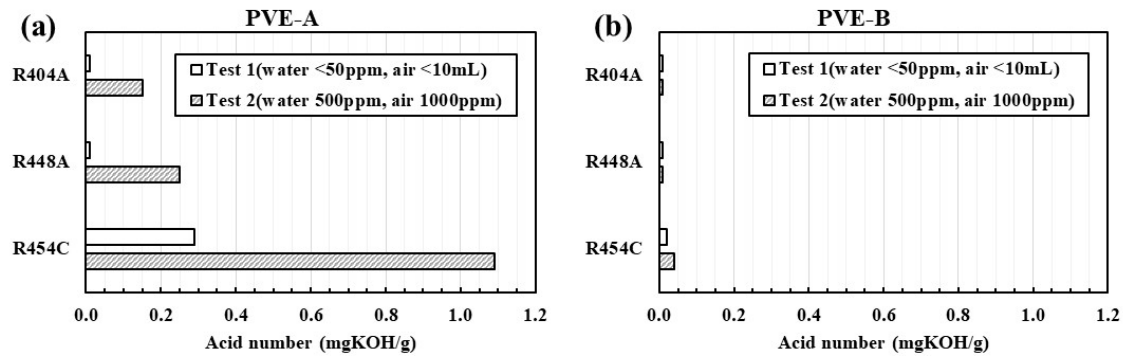
## 3. RESULTS AND DISCUSSIONS

### 3.1 Thermal Stability of Pure Oil and refrigerant Mixtures

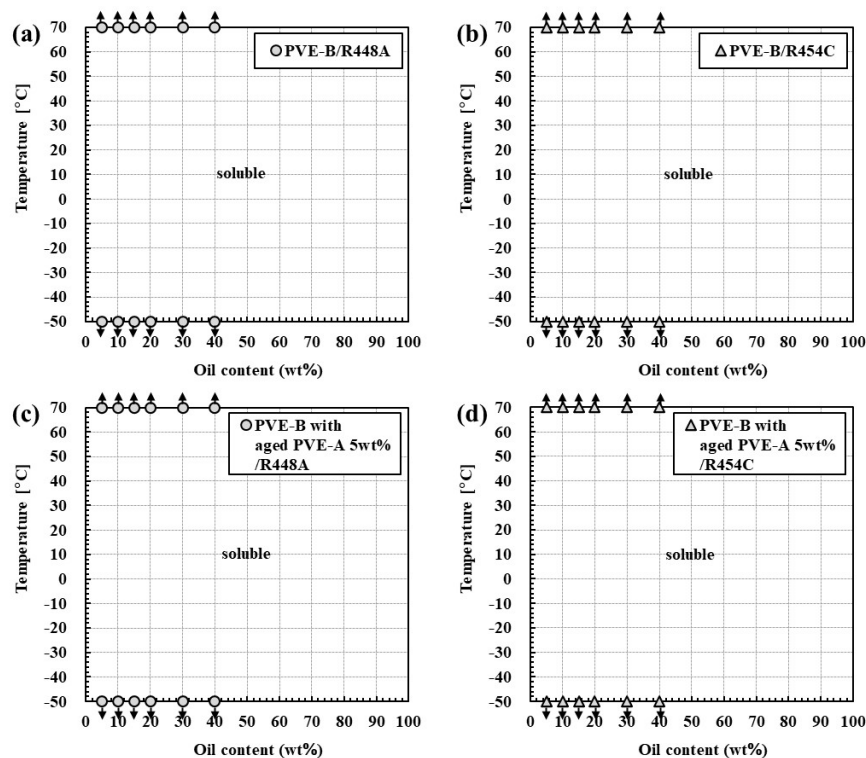
Prior to evaluating the contaminated oil, thermal stability tests were performed on the two types of refrigeration oil samples, PVE-A and PVE-B, under HFC and HFO refrigerant atmospheres. The tests were conducted under two conditions: Test 1, which did not include water and air, and Test 2, which included both water and air. As degradation of refrigeration oil progresses, acidic components are generated. Therefore, in this study, the thermal stability of the oil was evaluated by measuring the acid number which is an indicator of the concentration of acidic components. Figure 5 shows the acid numbers of the oils obtained from the thermal stability tests. While PVE-A/R404A shows the low acid numbers in Test 1, its acid number increased to 0.15 mgKOH/g in Test 2, indicating the presence of water and air accelerates the degradation of oil and refrigeration mixtures. The acid number of PVE-A/R448A in Test 2 was higher compared to PVE-A/R404A. Furthermore, PVE-B/R454C showed even higher acid numbers in both Test 1 and Test 2, confirming that HFO refrigerants accelerated degradation more than HFC refrigerants. Additionally, the higher acid numbers with R454C compared to R448A is likely due to its higher content of HFO refrigerant components. In contrast, even under Test 2 conditions, PVE-B exhibited very low acid numbers with both HFC and HFO refrigerants, confirming its exceptionally high thermal stability. This indicates that the stabilizer included in PVE-B effectively suppresses the increase in acid number. Therefore, it is necessary to use refrigeration oils formulated with appropriate additives that can counteract the poor thermal stability of HFO refrigerants. A small amount of aged PVE-A/R404A from Test 2 was mixed into PVE-B to prepare the samples for subsequent evaluation.

### 3.2 Miscibility of Contaminated Oil and HFO Refrigerant

The miscibility of refrigeration oil and refrigerant was evaluated based on the two-phase separation temperature. The separation temperature was measured for samples with oil contents of 5-40% within a temperature range of -50°C to 70°C. For both PVE-B/R448A and PVE-B/R454C, no separation regions were observed throughout the entire regions, confirming high miscibility with HFO refrigerants (Figure 6). Subsequently, the miscibility of PVE-B contaminated with 5wt% aged PVE-A was evaluated. The results showed that the miscibility was similar to that of the pure oil throughout the entire ranges in both cases with R448A and R454C. Thus, there was no significant impact on the miscibility even when PVE-A, used under HFC conditions, contaminated the PVE-B/HFO system.



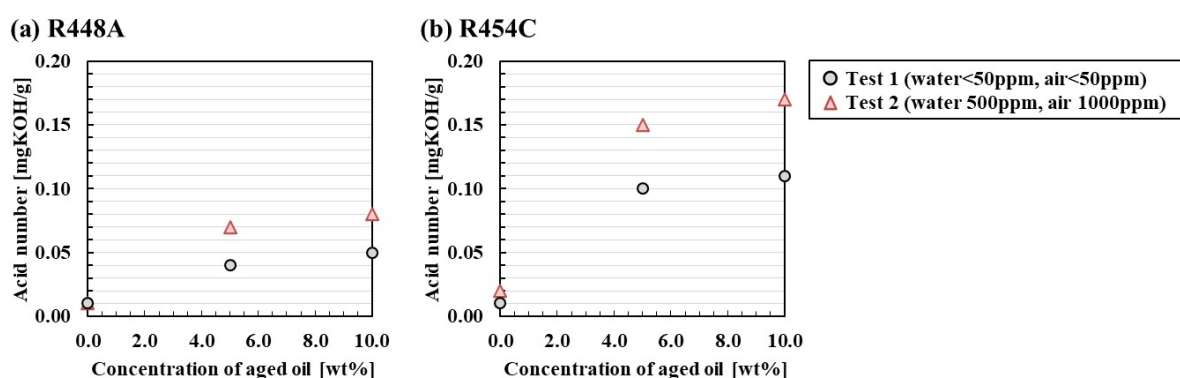
**Figure 5:** Acid number of (a) PVE-A and (b) PVE-B after thermal stability test under the refrigerants at 175°C for 336 h in the presence of metal catalyst.



**Figure 6:** Two-phase separation temperature of (a) PVE-B/R448A, (b) PVE-B/R454C, (c) PVE-B contaminated with 5wt% aged PVE-A/R448A, and (d) PVE-B contaminated with 5wt% aged PVE-A/R454C. The upward and downward arrows indicate a two-phase separation temperature above 70°C and below -50°C, respectively.

### 3.3 Thermal Stability of Contaminated Oil and HFO Refrigerant Mixtures

Finally, the thermal stability of the contaminated oils was evaluated. Thermal stability tests were conducted on PVE-B contaminated with 5% and 10% aged PVE-A under both R448A and R454C conditions. Notably, the acid numbers of the 5% and 10% contaminated oils before the tests were 0.02 and 0.03 mgKOH/g, respectively. Figure 7 summarizes the increase in acid number after the tests. In the case of R448A, while there was no increase in acid number with increasing contamination levels in Test 1, only a slight increase was observed in Test 2, suggesting the small impact of contamination on thermal stability. For R454C, the contaminated oils exhibited higher acid numbers compared to those with R448A, indicating that the impact of aged oil on thermal stability is relatively significant under the refrigerant with high HFO component ratio. The increase in acid number under R454C for the contaminated oil was less than that of pure PVE-A/R404A after testing, as shown in Figure 4. This suggests that PVE-B, involving the appropriate stabilizer, contaminated with aged PVE-A exhibits sufficient thermal stability for practical performance. However, as the acid number increases with the contamination level under HFO conditions, it is crucial in the drop-in approach from HFC to HFO refrigerants to minimize residual oils as much as possible through adequate flushing.



**Figure 7** Acid number of PVE-B contaminated with aged PVE-A after thermal stability test under the refrigerants in the presence of metal catalyst at 175°C for 336 h.

## 4. CONCLUSIONS

In this study, we conducted miscibility and thermal stability tests to evaluate the impact of residual oil contamination on the robustness of refrigeration oils in a drop-in approach from HFC to HFO refrigerants. We confirmed that the contamination of PVE-A aged under R404A does not significantly affect the miscibility with PVE-B and HFO refrigerants. However, the contamination slightly reduces thermal stability under HFO conditions, indicating that employing the appropriate stabilizer as an additive for refrigeration oils is critical for the oils intended for HFO refrigerants.

## NOMENCLATURE

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

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