Performance Evaluation of Refrigeration Lubricants Containing Fluorescent Dye for Refrigerant Leak Detection.

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ABSTRACT

High global-warming-potential (GWP) refrigerants are a major climate concern; reducing their emissions from refrigeration and air-conditioning systems is essential. Efficient methods for early leak detection during system operation have therefore been proposed. These include gas detection methods, remote monitoring based on operation data, and the fluorescent dye method, in which fluorescent dye–containing refrigeration lubricants are injected into the system and leak points are located under ultraviolet (UV) illumination. In this report, we investigated fluorescent dye–containing refrigeration lubricants with various refrigerants by evaluating fluorescence intensity and lubricant–refrigerant mixture performance, including thermal stability, oxidation stability, and miscibility.

Keywords: Refrigeration Lubricant, Fluorescent Dye, Refrigerant Leak detection, Miscibility, Stability

1. INTRODUCTION

Refrigerants such as R404A, R410A, R134a, and R32, which are currently used in refrigeration systems and car air conditioners, have an ozone depletion potential (ODP) of 0. However, they still have high global warming potentials (GWP) and have been targeted for reduction under the Kigali Amendment to the Montreal Protocol in 2016. In Japan, the Act on Rational Use and Proper Management of Fluorocarbons and other regulations have established the target GWP values and deadlines for various product categories. Consequently, refrigerant manufacturers have proposed a variety of low-GWP refrigerants, and equipment manufacturers are actively exploring the use of these alternative refrigerants.

Meanwhile, many refrigeration systems employing high GWP refrigerants remain in service, and mitigating refrigerant leakage from such systems is a major challenge. Because most refrigerant leakages occur during operation, refrigeration and air-conditioning equipment is subject to routine checks and periodic inspections. Methods for the early detection of refrigerant leaks—such as gas detection and remote monitoring based on operation data—have been proposed and implemented. More recently, the fluorescent dye method has attracted increasing attention. In this method, a small amount of fluorescent dye-containing refrigeration lubricant is injected into the system, after which the system is operated. Then the dye released with the refrigerant at leak sites is detected under ultraviolet (UV) illumination.

Because fluorescent dyes are not components of conventional refrigeration lubricants, they may affect both system performance and lubricant properties, including chemical stability and miscibility. Therefore, we developed a concentrated additive, designated PVE68-DY, in which the fluorescent dye is pre-diluted with polyvinyl ether (PVE). This additive was designed to maintain lubricant stability and miscibility even when further diluted with conventional refrigeration lubricants [1].

In this study, we investigated fluorescent dye–containing refrigeration lubricants, including PVE68-DY, with various refrigerants, focusing on fluorescence intensity and lubricant–refrigerant mixture performance: thermal stability, oxidation stability, and miscibility.

2. EXPERIMENTAL

2.1 Lubricants and Refrigerants

The general chemical structure of PVE is shown in Figure 1.

Table 1 presents the general properties and additive composition of the PVE refrigeration lubricants. PVE68A and PVE56B were formulated for HFC and HFO refrigerants, respectively.

The refrigerants R32, R454B, and R1234yf were employed in this study, and their GWP and respective compositions are shown in Table 2.

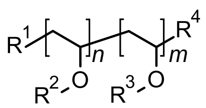

Figure 1 Chemical Structure of PVE

Table 1 Specification of PVEs

Lubricant		PVE68A	PVE56B
Application		HFCs	HFOs
Viscosity @40°C (mm^2/s)		64.0	55.6
Viscosity @100°C (mm^2/s)		8.0	7.3
Viscosity Index		89	90
Acid Number (mgKOH/g)		0.01	0.01
Density@ 15°C (g/cm^3)		0.944	0.936
Volume Resistivity@RT(Ω･m)		10^{12}	10^{12}
additive	antiwear	include	include
	antioxidant	include	include
	acid scavenger	include	include
	stabilizer	-	include

Table 2 Specification of Refrigerants

Refrigerant			R32	R454B	R1234yf
GWP(AR4)			675	466	4
Refrigerant Component (wt%)	R32	CH_2F_2	100	68.9	-
	R1234yf	$CF_3CF=CH_2$	-	31.1	100

2.2 Fluorescence Intensity Test

The experimental setup for the fluorescence intensity test is illustrated in Figure 2. A 5 μL drop of the test sample was placed on a copper plate, and its appearance observed under UV light irradiation in ambient lighting at source-to-sample distances of 38 and 100 cm. UV irradiation was carried out using a UV lamp (wavelength: 365 nm, nominal irradiance: 30,000 μW cm^{-2} at 38 cm). Fluorescence intensity was assessed qualitatively by visual observation.

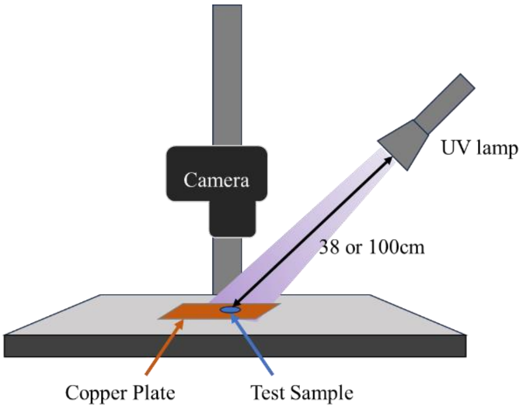

Figure 2 Experimental Setup for the Fluorescence Intensity Test

2.3 Stability Test

The stability of various lubricant-refrigerant mixtures was evaluated with the autoclave test. Table 3 presents the test conditions. In Test 1, thermal stability was evaluated by eliminating the influence of moisture and air. In Test 2, oxidative and hydrolytic stability was evaluated by adding moisture and air. After the autoclave tests, the samples were evaluated with respect to their acid number. To assess whether the fluorescence intensity was retained after the stability test, each sample containing 1wt% PVE68-DY was irradiated with UV light at 100 cm, and the fluorescence intensity was observed.

Table 3 Stability Test Conditions

Conditions	Test1	Test2
ure (℃)	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

2.4 Miscibility Test

The miscibility of refrigeration lubricant and refrigerant is evaluated by measuring the two-phase separation temperature. Figure 3 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 due to clouding was defined as the critical separation temperature (CST). A phase-separation diagram was generated based on the CSTs at various oil contents [2].

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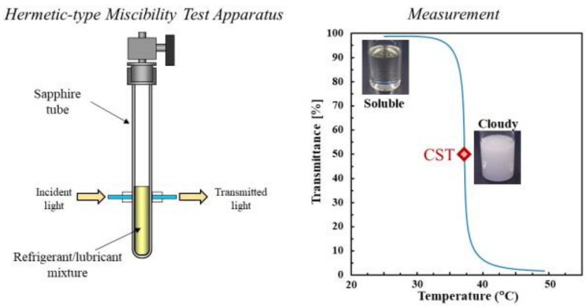


Figure 3 Miscibility Test Apparatus and Method

3. RESULTS AND DISCUSSION

3.1 Properties of Diluted Fluorescent Dye-Containing Lubricants

Table 4 shows the appearance of PVE68-DY under ambient lighting and under UV irradiation. Under ambient lighting, it appears colorless and transparent, whereas it emits blue fluorescence under UV irradiation.

Dye-containing samples were prepared by diluting PVE68-DY with two grades of PVE refrigeration lubricants. Table 5 summarizes their properties. The mass ratio of PVE68-DY is indicated at the end of the sample name. For example, PVE68A-10 represents a mixture consisting of 90wt% PVE68A and 10% PVE68-DY. The measured properties of all samples, including viscosity, acid number, density, and volume resistivity, were comparable to those of the corresponding fluorescent dye–free lubricants PVE68A and PVE56B.

Table 4 Appearance of PVE68-DY

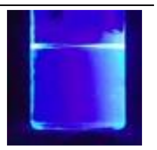
PVE68-DY Appearance	
under ambient lighting	under UV irradiation
	
Transparent	Blue emission

Table 5 Properties of Diluted PVEs

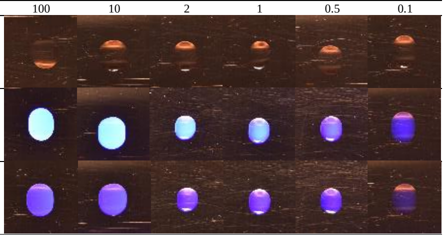
Test Sample		PVE68A-10	PVE68A-1	PVE56B-10	PVE56B-1
Mass Ratio	PVE68A or PVE56B	90	99	90	99
wt%	PVE68-DY	10	1	10	1
Viscosity @40°C (mm^2/s)		63.8	63.5	56.6	55.7
Viscosity @100°C (mm^2/s)		8.0	8.0	7.4	7.4
Viscosity Index		89	90	90	90
Acid Number (mgKOH/g)		0.01	0.01	0.01	0.01
Density@ 15°C (g/cm^3)		0.944	0.944	0.937	0.936
Volume Resistivity@RT(Ω・m)		10^{12}	10^{12}	10^{12}	10^{12}

3.2 Fluorescence Intensity Test

In localizing refrigerant leaks using a fluorescent dye, the fluorescence intensity of the dye-containing lubricant and the observable distance are critical. Accordingly, we evaluated the effect of PVE68-DY concentration on fluorescence intensity. Test samples were prepared with PVE68-DY mass fractions ranging from 100 down to 0.1wt%.

Table 6 presents the results of fluorescence intensity test. The fluorescence intensity of PVE68A-10 was comparable to that of PVE68-DY; however, a moderate attenuation in intensity was observed upon further dilution. Nevertheless, even at a dye content of 0.5 wt%, distinct fluorescence was clearly detectable at an irradiation distance of 100 cm. At concentrations below 0.5 wt%, fluorescence visibility at 100 cm deteriorated, and at 0.1 wt%, only faint fluorescence was detectable. Thus, we decided that the minimum PVE68-DY concentration required to secure sufficient visibility is 0.5wt%.

Table 6 Results of Fluorescence Intensity Test

Test Sample		PVE68-DY	PVE68A-10	PVE68A-2	PVE68A-1	PVE68A-0.5	PVE68A-0.1
Mass Ratio	PVE68A or PVE56B	0	90	98	99	99.5	99.9
wt%	PVE68-DY	100	10	2	1	0.5	0.1
No UV irradiation							
UV exposure distance cm	38						
	100						

3.3 Stability Test

Because the fluorescent dye concentration in the lubricant may decrease during actual service, stability tests were carried out using samples containing 1wt% PVE68-DY, a level considered adequate to maintain visibility even under conditions leading to dye depletion.

In practical applications, dilution of fluorescent dye–containing lubricants may lead to excessive dye content, which could potentially affect lubricant stability. To assess this, additional samples were evaluated: for R32, PVE68A-10; for R454B and R1234yf, PVE56B-10. Figure 4 presents the acid numbers of the samples following the stability test with R32, and Table 7 summarizes the fluorescence intensity of PVE68A-1 after testing. In Test 1, the increase in acid number was negligible for all samples. In Test 2, a slight increase in acid number was observed; however, the values for PVE68A-10, and PVE68A-1 were comparable to that of the dye-free base lubricant PVE68A, indicating that the addition of the fluorescent dye did not impair stability. Furthermore, the fluorescence intensity of the PVE68A-1 was maintained under all conditions after the tests.

Figure 5 and Tables 8 and 9 summarize the results of the stability tests performed with R454B and R1234yf. In both cases, trends were like R32: acid number increases were comparable to the dye-free lubricant, and fluorescence intensity was maintained after testing.

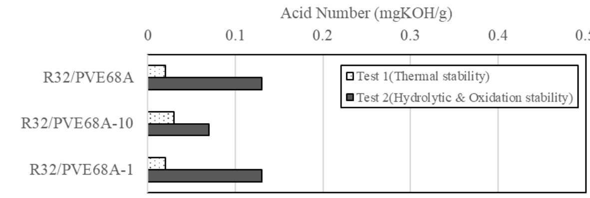
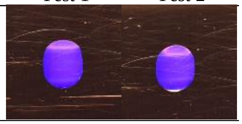


Figure 4 Acid Numbers after the Stability Tests with R32

Table 7 Fluorescence Intensity of PVE68A-1 after the Stability Tests with R32

Sample	PVE68A-1	
Refrigerant	R32	
Condition	Test 1	Test 2
under UV (100cm) Appearance		

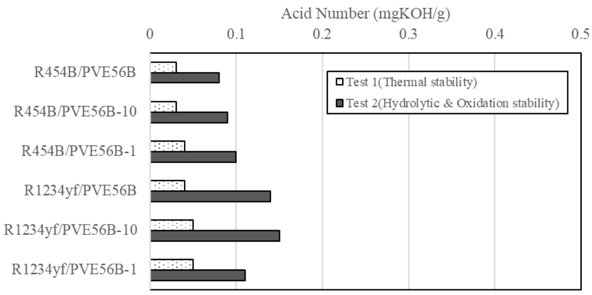


Figure 5 Acid Numbers after the Stability Tests with R454B and R1234yf

Table 8 Fluorescence Intensity of PVE56B-1 after the Stability Tests with R454B

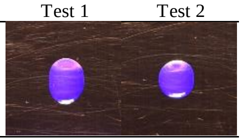
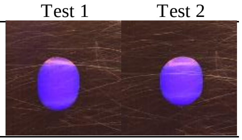
Sample	PVE56B-1	
Refrigerant	R454B	
Condition	Test 1	Test 2
under UV (100cm) Appearance		

Table 9 Fluorescence Intensity of PVE56B-1 after the Stability Tests with R1234yf

Sample	PVE56B-1	
Refrigerant	R1234yf	
Condition	Test 1	Test 2
under UV (100cm) Appearance		

3.4 Miscibility Test

Excessive fluorescent dye may adversely affect miscibility or cause precipitation at low temperatures. Therefore, as in the stability test, samples with high dye concentrations were evaluated.

Figures 6, 7, and 8 present the results of the miscibility tests conducted with R32, R454B, and R1234yf, respectively. For R32, CSTs for all samples, including those with PVE68A-10, were nearly identical to dye-free PVE68A. Furthermore, no precipitation of the fluorescent dye was observed at −50 °C for any oil content examined. The similar tendency was observed in the R454B and R1234yf systems: their CSTs were equivalent to that of the dye-free lubricant, PVE56B, and no low-temperature precipitation of the dye was detected.

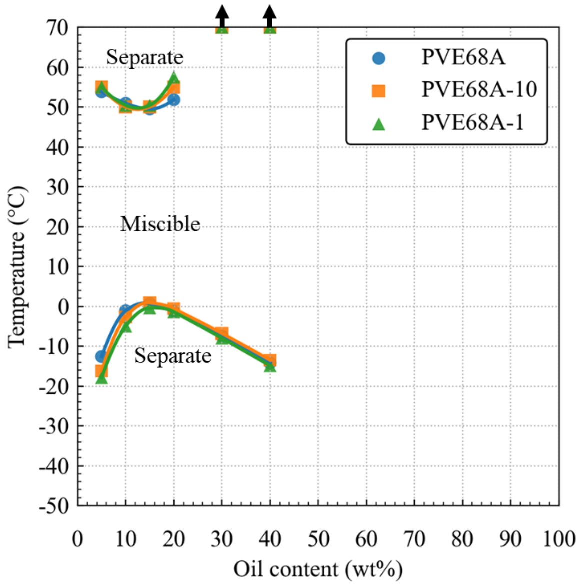


Figure 6 CST diagrams for PVE-R32

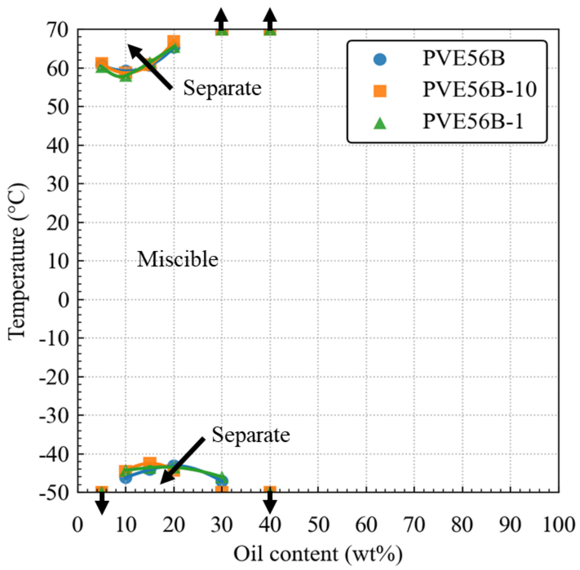


Figure 7 CST diagrams for PVE-R454B

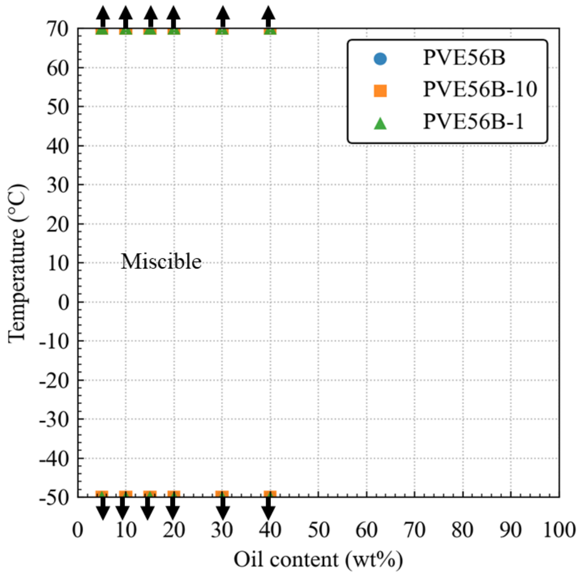


Figure 8 CST diagrams for PVE-R1234yf

4. CONCLUSIONS

To verify whether the addition of a fluorescent dye affects lubricant performance, the developed fluorescent dye-containing refrigeration lubricant (PVE68-DY) was diluted with PVE lubricants and evaluated with respect to fluorescence intensity, stability, and miscibility with the refrigerant. The results clearly demonstrated that PVE68-DY can be used in the PVE lubricants formulated for HFC and HFO-blend refrigerants without any deterioration in performance.

5.REFERENCES

[1] T. Matsumoto, N. Takagishi: Proc. 2022 JSRAE Annual Conference, JSRAE, (2022), E132. (in Japanese)

[2] Patent JP2823123