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Development of Polyol Ester Refrigeration Oils for HFO Refrigerants

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ABSTRACT

Recently, R32 refrigerant, which has low global warming potential (GWP), attracts much attention as an alternative one instead of R410A and has started to be used in practical systems of room air conditioners (RAC), but compared with natural refrigerants, its GWP of 675 is still high and it is required to use refrigerants with much lower GWP. In addition, although R134a (GWP=1300) is widely used for mobile air conditioner systems (MAC), it has been decided by MAC directive in Europe that refrigerants whose GWP is over 150 can no longer be available in future. In such a situation, HFO refrigerants like R1234yf, R1234ze (E) and an HFO-1123+R32 mixture are considered as the candidates for next-generation refrigerants because of their much lower GWP. Therefore, at the same time, it is required to develop refrigeration oils which have good compatibility with HFO refrigerants for RAC.
One of the characteristics of HFO refrigerants is that their miscibility with refrigeration oils is equal to or greater than that of HFCs. However, a problem is that HFOs have a double bond in their molecular structure, resulting in their lower chemical stability than that of HFCs. We developed polyol ester (POE) refrigeration oils with high chemical stability under HFO atmospheres by improving the formulation of additives. In this study, we will report the method and the characteristics of lubricity under HFOs.

1. INTRODUCTION

Efforts to prevent climate change are gaining momentum worldwide. At COP21 in 2015, the Paris Agreement was adopted, which includes targets for reducing emissions of greenhouse gases. R32, an HFC refrigerant which has recently started to be used in room air conditioning systems, has the advantage of a global warming potential (GWP) that is roughly one-third that of R410A. However, at 675, its GWP is still relatively high compared to natural refrigerants. Thus, hydrofluoroolefin (HFO) refrigerants, which have much lower GWPs, have attracted much attention as next-generation refrigerants that could be used in the fight against climate change.
Such being the case, new refrigeration oils must be developed which have good compatibility with HFO refrigerants. In this study, we report on how the solubility, lubricity, and chemical stability of polyol ester (POE) refrigeration oils are affected by exposure to HFO refrigerants such as R1234yf, R1234ze(E), and an HFO-1123+R32 mixture (Fukushima and Hashimoto, 2014), and compare these effects to those of exposure to hydrofluorocarbons (HFCs). In addition, we report on the development of a new POE oil which shows good performance with HFOs.

2. EXPERIMENTAL

The miscibility of samples was evaluated by the method specified in JIS K2211. The chemical stability of samples was evaluated by the autoclave test specified in JIS K2211. The measurements of both refrigerant concentration in oil and the kinematic viscosity of oil/refrigerant mixtures were carried out using the device shown in Fig. 1. Refrigerant and oil were put into a pressure vessel and heated to the target temperature. Kinematic viscosity was measured after adjusting the amount of refrigerant to being the pressure to the target level. The amount of refrigerant ratio in the oil was calculated from the weights of refrigerant and oil in the vessel. The kinematic viscosity of the oil/refrigerant mixture was measured by a viscosity sensor attached to the vessel. Lubricity was evaluated using the Falex Pin and Vee Block test machine in accordance with ASTM D2670, as refrigerants were bubbled into the oils.

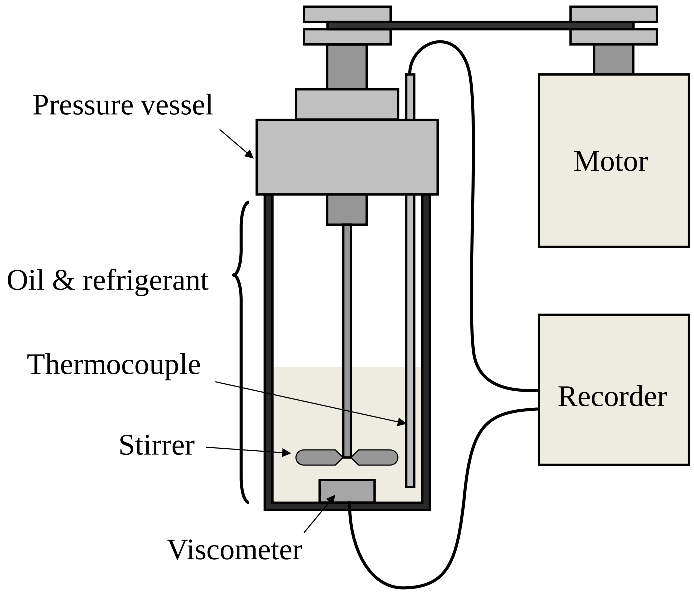

Figure 1: Schematic of equipment for viscosity measurement of refrigerant/refrigeration oil mixtures

3. CHARACTERISTICS OF HFO REFRIGERANTS

3.1 Miscibility

First, we tested the miscibility of POE oils with an HFO refrigerant, and with a current HFC refrigerant, R410A, for comparison. We used R1234yf as the HFO refrigerant to clarify the problems associated with HFOs. POE A, which is a mixture of esters derived from pentaerythritol, isooctanoic acid and isononanoic acid, was used as the refrigeration oil. We chose this POE oil because it is widely used for current R410A refrigeration systems. The characteristics of POE A are shown in Table 1. As shown in Fig. 2, the maximum value for phase separation temperature (PST) was 11 °C in the case of POE A/R410A. Meanwhile, the PST of POE A/R1234yf was below −60 °C, much lower than that of POE A/R410A. From these results, it was determined that the HFO refrigerant had better miscibility with POE A than did the HFC refrigerant.

Table 1: Characteristics of POE A

Oil			**POE A**
Viscosity grade			VG68
Kinematic viscosity	40 °C	mm^2/s	66.5
	100 °C	mm^2/s	8.2

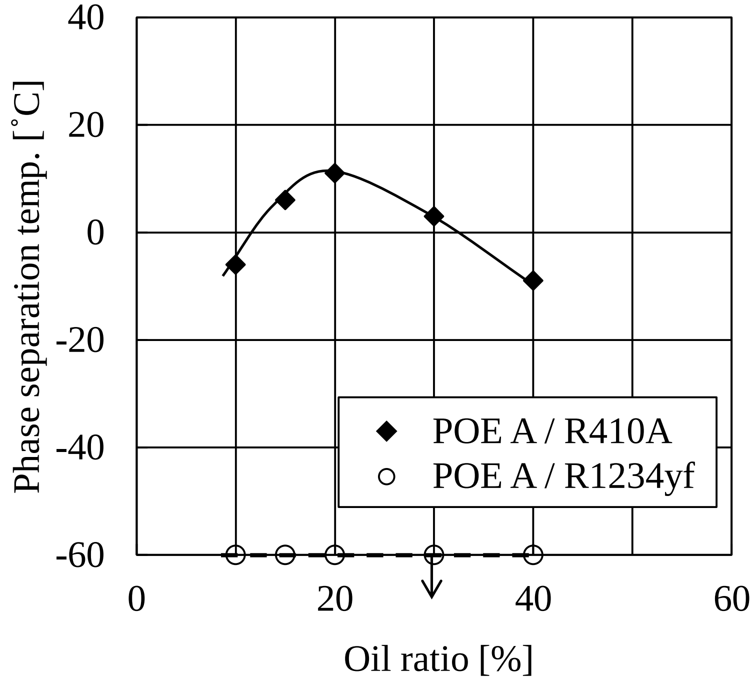

Figure 2: Miscibility of POE A with R410A and R1234yf

3.2 Lubricity

Second, we measured the lubricity of POE A under refrigerant atmospheres. The kinematic viscosities of the POE A/refrigerant mixtures and the results of lubricity tests with the Falex Pin and Vee Block test machine are shown in Table 2. Despite the fact that the kinematic viscosity of POE A/R1234yf was lower than that of POE A/R410A, the total wear of the pin and the block was less when bubbling with R1234yf than with R410A. This could be due to the higher reactivity of R1234yf with Fe and the consequent increased formation of iron fluoride on the sliding surfaces. These results indicate that the anti-wear properties of HFOs are higher than those of HFCs.

Table 2: Results of lubricity tests

Oil			**POE A**	
Refrigerant			R410A	R1234yf
Kinematic viscosity of oil/refrigerant mixture	40°C, 0.5 MPa	mm^2/s	38	19
Wear amount (pin + vee block)		mg	13.3	11.7

Load: 300 lb, time: 60 min, flow rate of refrigerant: 10 L/h

3.3 Stability

Next, we evaluated the chemical stability of the POE oils under R1234yf atmosphere. Because POE can undergo hydrolysis in the presence of large amounts of water, 1,000ppm of water was added to the oils prior to testing. And in light of the fact that problems can be caused by air getting into the system when air conditioning systems are built, 90 cc of air was added to the autoclave for the tests. The oils tested were POE A, which contained no anti-wear additives, and POE B, a POE oil formulated with anti-wear additives that is commonly used for R410A systems.

The results of the stability tests are shown in Table 3. While the acid number of POE A did not increase significantly under R410A, it did under R1234yf, and F^- ions were detected in the oil. It was assumed that radicals generated by the degradation of the oil had attacked the R1234yf, leading to formation of hydrogen fluoride. This hydrogen fluoride then accelerated the hydrolysis of the POE (Fujitaka *et al.*, 2010). In the case of POE B, the acid number increased under both refrigerants, but the value rose much higher under the R1234yf atmosphere. We found that the

anti-wear additive in the oil had been consumed during the test. This could mean that the anti-wear additive is easily decomposed under R1234yf atmosphere, leading to accelerated degradation of the refrigeration oil.
It was thus found that under an R1234yf and air atmosphere, the decomposition of R1234yf and the anti-wear additive could accelerate the degradation of POE oils. Contamination by air does not occur in refrigeration systems in normal operation, but considering such a possibility, we set out to optimize the additive package so as to make the oil more chemically stable when contaminated by air.

Table 3: Results of stability tests for POE A and POE B

Oil		**POE A**		**POE B**	
Refrigerant		R410A	R1234yf	R410A	R1234yf
Water	ppm	1,000			
Air	cc	90			
Acid number	mgKOH/g	0.24	0.67	1.58	4.29
F^- ions in oil	ppm	<1	8	<1	29
AW additive remaining	%	-	-	90	<10

Temperature: 175°C, time: 168 h, vessel volume: 200 mL, oil: 30 g, refrigerant: 30 g, catalyst: Fe, Cu, Al.

4. OPTIMIZATION OF ADDITIVES

4.1 Optimization of Stabilizers

The first step was to optimize the stabilizer. POE B' was prepared by utilizing a different stabilizer with higher reactivity with HF and optimizing its amount. The stability test for POE B'/R1234yf is shown in Table 4. POE B' showed a smaller acid number increase under R1234yf than did POE B. It was thus found that the acid number increase could be limited to some extent by changing the stabilizer, but it was still higher than that of POE B under R410A. Therefore, we tried to further improve chemical stability.

4.2 Optimization of Anti-wear Additives

As mentioned above, sufficient chemical stability could not be achieved through optimization of the stabilizer alone. Having learned from the stability test results for POE B under R1234yf that the anti-wear additive also plays a role in chemical stability, we set about optimizing the anti-wear additive. POE C was prepared using a different type of anti-wear additive from the one used in POE B. This new anti-wear additive provides good anti-wear properties even when used in small amounts. The result of the stability test for POE C, formulated with this new additive, is shown in Table 4. POE C showed a smaller acid number increase under R1234yf than did POE B under R410A. Meanwhile, the result of the Falex Pin and Vee Block anti-wear test of POE C with R1234yf is shown in Figure 3. The total wear of the pin and block with POE C/R1234yf was smaller than that with POE B/R410A. It was thus shown that POE C has high chemical stability and lubricity.

Table 4: Results of stability tests with POE B' and POE C

Oil		**POE B**		**POE B'**	**POE C**
Refrigerant		R410A	R1234yf		
Water	ppm	1,000			
Air	cc	90			
Acid number	mgKOH/g	1.58	4.29	3.15	1.01

Temperature: 175°C, time: 168 h, vessel volume: 200 mL, oil: 30 g, refrigerant: 30 g, catalyst: Fe, Cu, Al.

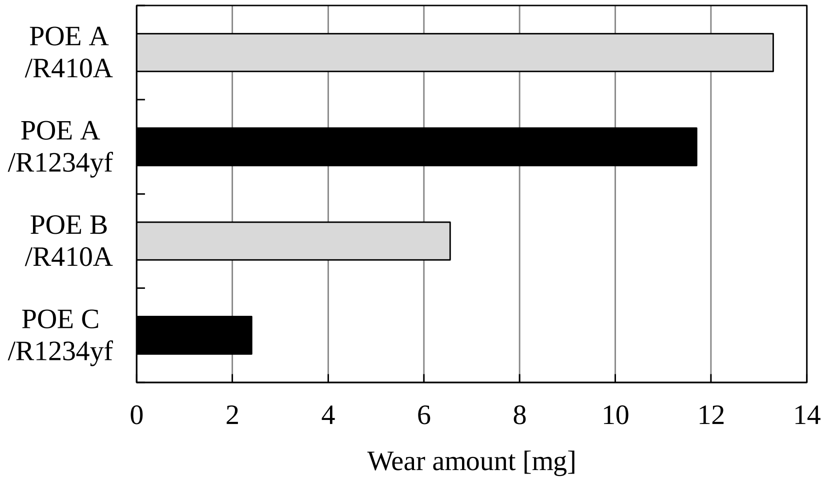

Figure 3: Lubricity of POE C with R1234yf

4.3 Characteristics of Newly Developed POE Oil with HFO Refrigerants

In order to clarify the problems associated with HFOs, we had been using a typical HFO, R1234yf, for the evaluation, and carried out chemical stability tests with air added, in consideration of the possibility that the oil could become contaminated by air. Through optimization of the POE additive package, we developed POE C, which has both high chemical stability, even under a mixed R1234yf and air atmosphere, and excellent lubricity. However, because contamination by air rarely occurs in refrigeration systems in normal operation, it made sense to perform the stability test without adding air in order to evaluate the true performance of the refrigeration oil. Therefore, we tested POE C under HFO refrigerants such as R1234yf, R1234ze(E), and an HFO-1123+R32 mixture assuming there would be no contamination by air.

First, the miscibility of POE C with the HFOs is shown in Figure 4. POE C showed lower PSTs with the HFOs than with R410A. This showed that POE C has better miscibility with not only R1234yf but also R1234ze(E) and an HFO-1123+R32 mixture than with the HFC refrigerant.

Next, the chemical stability and lubricity test results for POE C under HFO atmospheres are shown in Table 5. The acid number of POE C did not increase in the stability tests with the HFOs, showing the high chemical stability of POE C. Moreover, total wear in the Falex Pin and Vee Block test was less with POE C bubbled with R1234ze(E) and the HFO-1123+R32 mixture than with POE B bubbled with R410A, which shows the excellent anti-wear properties of POE C. In addition, as Table 5 shows, we found that POE C has good chemical stability and anti-wear properties even under the HFC refrigerant, R410A.

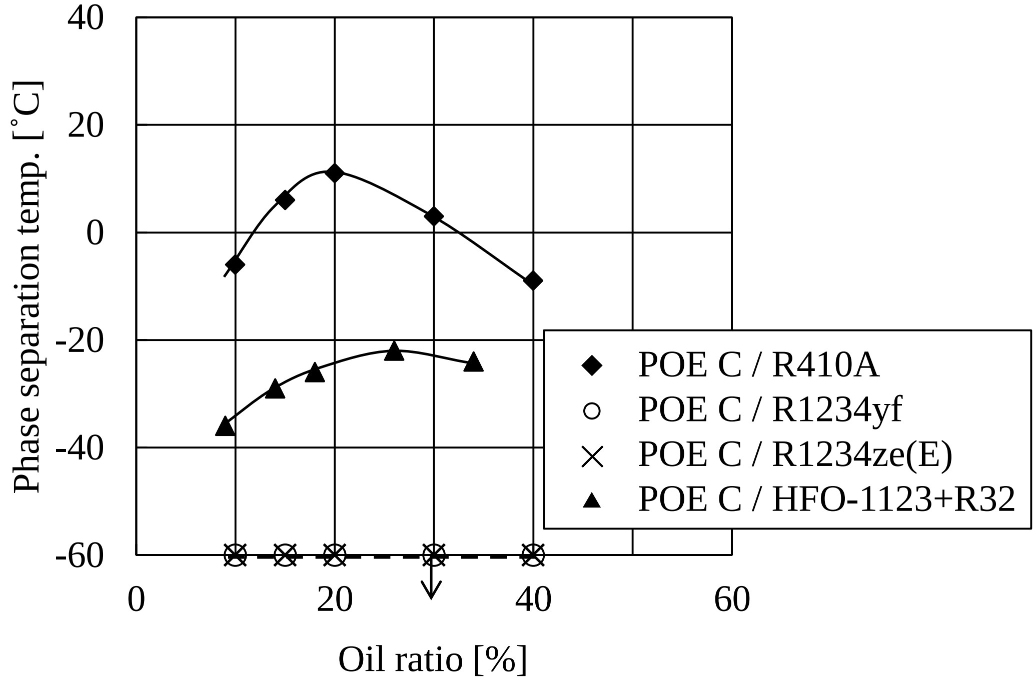

Figure 4: Miscibility of POE C with HFO refrigerants

Table 5: Stability and lubricity of POE C with HFO refrigerants

Oil		**POE C**			
Refrigerant		R1234yf	R1234ze(E)	HFO-1123+R32	R410A
Acid number (after stability test)[1]	mgKOH/g	0.01	0.01	0.02	0.01
Wear amount (pin + vee block)[2]	mg	2.4	2.4	2.7	3.6

1. Temperature: 175°C, time: 168 h, vessel volume: 200 mL, oil: 30 g, refrigerant: 30 g, water: 1,000ppm, air: 0 cc, catalyst: Fe, Cu, Al.
2. Load: 300 lb, time: 60 min, flow rate of refrigerant: 10 L/h

5. CONCLUSIONS

- It was demonstrated that HFO refrigerants have better miscibility and better lubricity with POE than do HFC refrigerants.
- In stability tests under an R1234yf and air atmosphere, the degradation of the POE oils was accelerated by the formation of hydrogen fluoride. But through optimization of the stabilizer and the anti-wear additive, we developed POE C, which has both high chemical stability and lubricity.
- POE C was shown to have high miscibility, lubricity, and chemical stability under HFO refrigerant atmospheres such as R1234yf, R1234ze(E), and an HFO-1123+R32 mixture.

NOMENCLATURE

GWP	global warming potential
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
MAC	mobile air conditioner
POE	polyol ester
PST	phase separation temperature

RAC room air conditioner

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