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# Properties of Polyol Esters for Low GWP Refrigerants

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## ABSTRACT

HFC (Hydrofluorocarbon) refrigerants, whose ODP (Ozone Depletion Potential) is 0, are used in refrigeration and air conditioning equipments recently. It is known that HFCs are high GWP (Global Warming Potential) refrigerants. In October 2016, Kigali Amendment to the Montreal Protocol was stated to achieve the phase-down of HFC refrigerants to prevent global warming. Transition of current HFCs to low GWP refrigerants would be accelerated around the world.

HFO (Hydrofluoroolefin) refrigerants such as R1234yf, R1234ze etc. are low GWP refrigerants. Refrigerant manufacturers are introducing not only HFO itself, but also mixture of HFC and HFO. HFO is known to be less chemically stable compared to HFC since there is double bond in its molecular structure. Also, HFOs tend to dissolve well with refrigeration oil compared to HFCs. As a result, amount of refrigerant dissolving in the oil increase and the kinematic viscosity of the oil decrease.

We investigated ways to solve problems which may occur by using HFOs. In particular, it is important to maintain the stability and lubricity of oil. To improve stability, we optimized the amount of the stabilizer. To improve lubricity, since the kinematic viscosity of the oil decrease because the refrigerant dissolve in the oil more than necessary, we applied original base oil formulation to prevent the refrigerant from dissolving too much to the oil. In the presentation, properties of POE refrigeration oils which solve problems of low GWP refrigerants by investigating appropriate base oil and additive formulation are introduced.

## 1. INTRODUCTION

Recently, efforts to prevent climate change are gaining worldwide. At COP21 in 2015, the Paris Agreement was adopted as a new framework to replace the Kyoto Protocol, which stated targets for each country to reduce emissions of greenhouse gases. In 2016, Kigali Amendment to the Montreal Protocol was stated to reduce usages of high GWP HFC refrigerants gradually (Kagawa, 2019). GWP of R32, a HFC refrigerant used in room air conditioning systems, is 675 which is roughly one-third of R410A whose GWP is 2088. However, GWP of R32 is still relatively high compared to the reduction target set by Kigali Amendment. Therefore, HFO refrigerants, which have much lower GWP, have attracted attentions as next-generation refrigerants.

In the previous paper, we reported the effects of HFO refrigerants on lubricity and chemical stability of POE refrigeration oils and how the effects on tribological properties varied among different refrigerants (Yamaguchi *et al.*, 2016). Since refrigerant manufacturers are introducing not only HFO itself, but also mixture of HFC and HFO, we have been investigating appropriate base oil and additive formulation of POE refrigeration oils for HFC/HFO mixed refrigerants. In this study, we report miscibility, Kinematic viscosity, lubricity, and chemical stability of POE refrigeration oils under the atmosphere of R454B, R454C, R463A, alternative refrigerants for R410A and R404A. In addition, we report the development of new POE oils which show good performance with HFC/HFO mixed refrigerants.

## 2. EXPERIMENTAL

The miscibility of samples was evaluated by the method specified in JIS K2211. The measurement of 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. The kinematic viscosity was measured after adjusting the amount of refrigerant to be the target pressure. 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. The chemical stability of samples was evaluated by the autoclave test specified in JIS K2211.

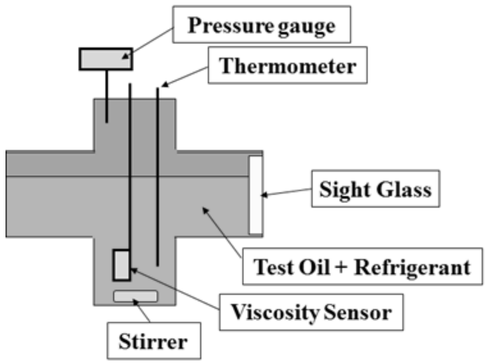


**Figure 1:** Schematic of equipment for viscosity measurement of refrigerant/refrigeration oil mixtures

## 3. CHARACTERISTICS OF POE OILS UNDER HFC/HFO MIXED REFRIGERANTS

### 3.1 Miscibility

First, we tested the miscibility of POE oils under HFC/HFO mixed refrigerants and compared it with the miscibility under HFC refrigerants. We used R454B, R463A as alternative refrigerants for R410A, and R454C as an alternative refrigerant for R404A. As for the refrigeration oil, we chose POE A which is widely used in current refrigeration systems. The characteristics of POE A are shown in Table 1. As shown in Fig. 2 and Fig. 3, POE A has better miscibility with HFC/HFO mixed refrigerants than with HFC refrigerant itself. This result indicates POE A could be applied not only to the current system with HFC refrigerants but also to the system with HFC/HFO mixed refrigerants. Also, POE A could widen its applicability to systems which require the refrigeration oil to dissolve well with refrigerants because of their wide temperature range.

**Table 1:** Characteristics of POE A

| **Oil** | | | **POE A** |
|---|---|---|---|
| Kinematic viscosity | 40 °C | $mm^2/s$ | 67.1 |
| | 100 °C | $mm^2/s$ | 8.3 |
| Viscosity Index | | | 91 |

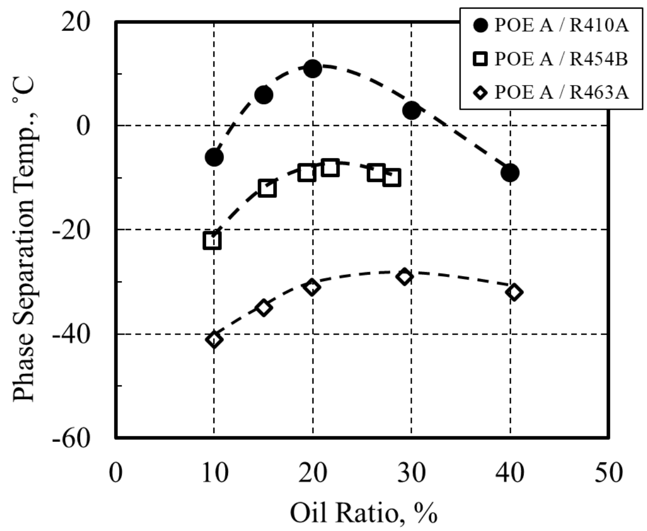


**Figure 2:** Miscibility of POE A with R410A, R454B and R463A

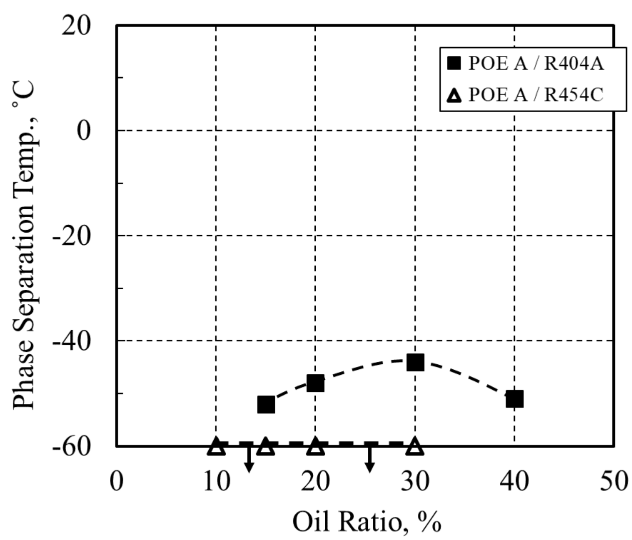


**Figure 3:** Miscibility of POE A with R404A and R454C

### 3.2 Kinematic Viscosity

The kinematic viscosities of POE A under refrigerant atmospheres were measured and are shown in Table 2, 3. Although same type of POE oil as POE A is already applied to some HFC/HFO mixed refrigerant systems, since POE A dissolves well with HFC/HFO mixed refrigerants, the kinematic viscosities under HFC/HFO mixed refrigerants tend to decrease compared to that of HFC refrigerants.

**Table 2:** Kinematic viscosities of POE A under R410A, R454B and R463A

| **Oil** | | | **POE A** | | |
|---|---|---|---|---|---|
| Refrigerant | | | R410A | R454B | R463A |
| Kinematic viscosity of oil/refrigerant mixture | 80°C, 3.4 MPa | $mm^2/s$ | 3.0 | 2.5 | 2.7 |

**Table 3:** Kinematic viscosities of POE A under R404A and R454C

| **Oil** | | | **POE A** | |
|---|---|---|---|---|
| Refrigerant | | | R404A | R454C |
| Kinematic viscosity of oil/refrigerant mixture | 80°C, 2.3 MPa | $mm^2/s$ | 3.9 | 2.6 |

# 4. OPTIMIZATION OF BASE OIL FORMULATION AND ADDITIVES

## 4.1 Optimization of Base Oil Formulation

The optimization of base oil formulation to maintain the kinematic viscosity under refrigerant atmosphere was investigated. POE B and POE C were prepared by utilizing several types of base oils as shown in Table 4.
First, miscibility and kinematic viscosity of POE B were tested. As shown in Fig. 4 and Fig.5, POE B has good miscibility with HFC/HFO mixed refrigerants like POE A does. Not only good miscibility but also, as shown in Table 5 and Table 6, the kinematic viscosity of POE B under R454B and R454C is same level as the kinematic viscosity of POE A under R410A and R404A.
Next, miscibility and kinematic viscosity of POE C were examined. As shown in Fig. 6, POE C has better miscibility with HFC/HFO mixed refrigerants than POE A does. Like in the case of POE B, the kinematic viscosity of POE C under R454B and R463A is same level as the kinematic viscosity of POE A under R410A as shown in Table 7.
These results indicate that POE B and POE C have good miscibility and high kinematic viscosity at the same time under HFC/HFO mixed refrigerants atmosphere.

**Table 4:** Characteristics of POE B and POE C

| **Oil** | | | **POE A** | **POE B** | **POE C** |
|---|---|---|---|---|---|
| Kinematic viscosity | 40 °C | $mm^2/s$ | 67.1 | 83.2 | 91.2 |
| | 100 °C | $mm^2/s$ | 8.3 | 10.6 | 11.4 |
| Viscosity Index | | | 91 | 111 | 113 |

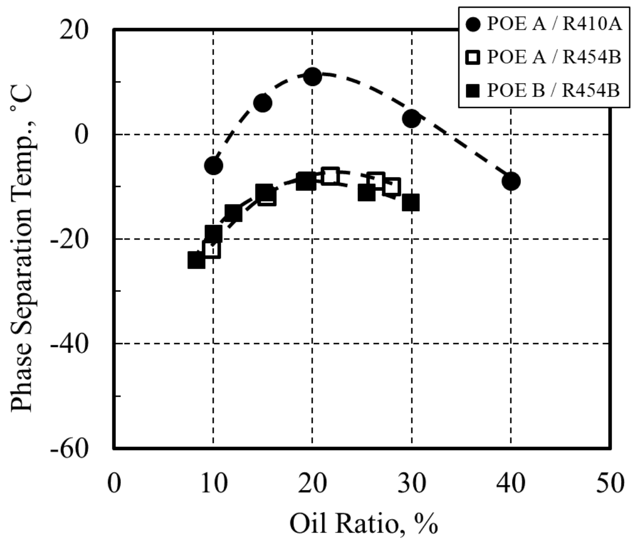


**Figure 4:** Miscibility of POE B with R454B

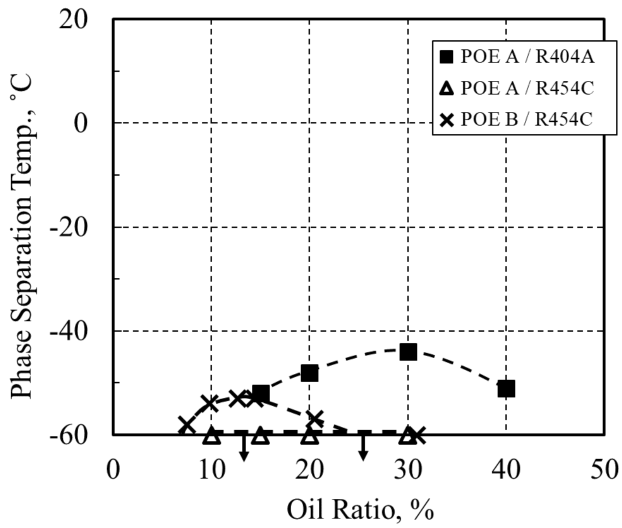


**Figure 5:** Miscibility of POE B with R454C

**Table 5:** Kinematic viscosities of POE B under R454B

| **Oil** | | | **POE A** | | **POE B** |
|---|---|---|---|---|---|
| Refrigerant | | | R410A | R454B | R454B |
| Kinematic viscosity of oil/refrigerant mixture | 80°C, 3.4 MPa | $mm^2/s$ | 3.0 | 2.5 | 3.2 |

**Table 6:** Kinematic viscosities of POE B under R454C

| **Oil** | | | **POE A** | | **POE B** |
|---|---|---|---|---|---|
| Refrigerant | | | R404A | R454C | R454C |
| Kinematic viscosity of oil/refrigerant mixture | 80°C, 2.3 MPa | $mm^2/s$ | 3.9 | 2.6 | 4.1 |

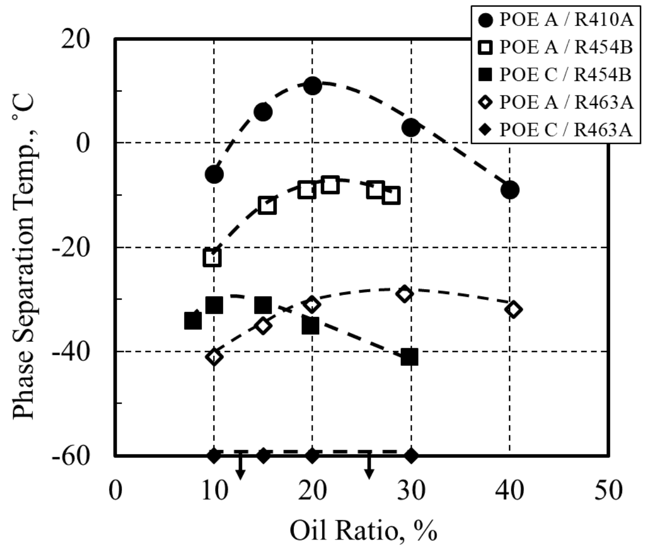


**Figure 6:** Miscibility of POE C with R454B and R463A

**Table 7:** Kinematic viscosities of POE C under R454B and R463A

| **Oil** | | | POE A | | | POE C | |
|---|---|---|---|---|---|---|---|
| Refrigerant | | | R410A | R454B | R463A | R454B | R463A |
| Kinematic viscosity of oil/refrigerant mixture | 80°C, 3.4 MPa | $mm^2/s$ | 3.0 | 2.5 | 2.7 | 3.2 | 3.4 |

## 4.2 Optimization of Additives

Next, optimization of additives was investigated as shown in Table 8. The Alphabet following the word POE indicates the base oil formulation and the number following the Alphabet indicates the additive package. POE A1, which does not contain anti-wear additives, has great stability under R410A atmosphere but wear amount of FALEX test was larger than POE A2, which contains anti-wear additive commonly used for HFC refrigerants systems. POE A2 showed great lubricity under R410A atmosphere but acid number after stability test was higher than POE A1. Since HFC/HFO mixed refrigerants include HFO refrigerant which is known to be less chemically stable compared to HFC refrigerants because of the double bond in its molecular structure and HFOs tend to dissolve well with refrigeration oil compared to HFCs, satisfying both stability and lubricity is assumed to be complicated. By optimizing the amount and type of stabilizer to improve stability and utilizing the anti-wear additive and the base oil formulation to improve lubricity, POE B3 and POE C3 developed. POE B3 showed great stability and lubricity under R454B and R454C atmosphere. POE C3 also showed great stability and lubricity under R454B and R463A atmosphere.

**Table 8:** Stability and lubricity of POE with each refrigerant

| **Oil** | | **POE A1** | **POE A2** | **POE B3** | | **POE C3** | |
|---|---|---|---|---|---|---|---|
| Refrigerant | | R410A | R410A | R454B | R454C | R454B | R463A |
| Acid number (after stability test)[1] | mgKOH/g | 0.01 | 0.60 | 0.02 | 0.04 | 0.02 | 0.01 |
| Wear amount (pin + vee block)[2] | mg | 13.3 | 6.6 | 1.5 | 6.7 | 2.6 | 3.0 |

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

- POE dissolves well with HFC/HFO refrigerants compared to HFC refrigerants.
- By optimizing the base oil formulation, POE B and POE C were developed which have good miscibility and high kinematic viscosity at the same time under HFC/HFO mixed refrigerants atmosphere.
- By utilizing the anti-wear and acid capture, POE B3 and POE C3 were developed which have great stability and lubricity under R454B and R454C atmosphere.

## NOMENCLATURE

| | |
|---|---|
| GWP | global warming potential |
| HFC | hydrofluorocarbon |
| HFO | hydrofluoroolefin |
| POE | polyol ester |

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