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Tribology Characteristics of HFO and HC Refrigerants with Immiscible Oils - Effect of Refrigerant with Unsaturated Bond -

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ABSTRACT

Hydrofluoroolefin (HFO) and hydrocarbon (HC) refrigerants have been considered for use in air-conditioning systems and refrigerators as low global warming potential (GWP) refrigerants. These refrigerants are determined the lubrication performance of the sliding parts in compressor. To clarify lubrication performance of unsaturated and saturated refrigerants for these low GWP refrigerants, seizure and wear tests were done in the compound of liquid refrigerant and refrigeration oil. For comparison with HFO-1234yf, which has an unsaturated bond, the lubrication performance of HFC-134a which has a saturated bond, was studied. R1270 (propylene), which has an unsaturated bond, and R290 (propane) were similarly studied as HC refrigerants. Immiscible oils to refrigerants were used for lubrication. We confirmed that antiwear and antiseizure characteristics of unsaturated refrigerants (HFO-1234yf and R1270) are better than those of saturated refrigerants HFC-134a and R290.

1. INTRODUCTION

HFO and HC refrigerants have been considered for use in air-conditioning systems and refrigerators as low GWP refrigerants. These refrigerants are determined the lubrication performance of the sliding parts in compressor. It is important to prevent the sliding parts from seizure and wear and to be ensured the reliability of equipments which are applied these refrigerants.

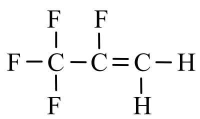
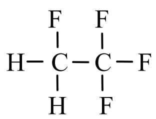
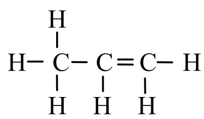
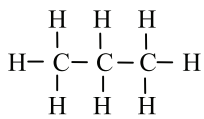
HFO-1234yf was developed from the joint research by Dupont and Honeywell. Minor (2008) outlined the thermodynamic characteristics and materials compatibilities of HFO-1234yf and its potential as a refrigerant alternative to HFCs. Benouali (2008) made a prediction of the life cycle climate performance (LCCP) for HFO-1234yf, but research reports about lubrication performance of HFO-1234yf have apparently not been published to date. On the other hand there are some reports about HC refrigerants, Sariibrahimoglu (2010) refers to tribological characteristics of sintered iron in R600a atmosphere. However the report concerning tribological characteristics is not seen the other.

The unsaturated refrigerant has a double bond in the molecular structure and can cause additional reactions, so it is expected to influence tribological characteristics in the reaction of oils or the sliding surface. Olivier (1996) studied the adsorption of propane and propylene, and clarified that adsorption increases in the presence of the unsaturated bond, but reports on tribological characteristics of unsaturated refrigerant are not seen. Here we discuss an experimental study of lubrication performance of low GWP unsaturated refrigerants. Sliding in mixtures of refrigerant and refrigeration oil were studied and sliding surface analysis done, and refrigerant stability studied.

2. REFRIGERANT AND REFRIGERATION OIL

Table 1 shows four refrigerants and their characteristics used in the seizure and wear tests. HFC-134a was selected as a saturated refrigerant to compare to unsaturated refrigerant HFO-1234yf. Physical properties of HFC-134a other than GWP such as thermal stability and material compatibility are similar to HFO-1234yf. R1270 (propylene) was selected as an unsaturated refrigerant of the HC refrigerant. R290 (propane) whose carbon number is equal to R1270 was selected as a saturated refrigerant. Immiscible oils maintaining viscosity when liquid refrigerant exists in the compressor were used for refrigeration oils. Alkyl benzene oil was used with HFCs and polyalkylene glycol oil was used with HCs. The ethylene oxide has been added to the propylene oxide in the polyalkylene glycol oil in order to reduce solubility with HC refrigerants.

Table 1: Refrigerant characteristics and combinations of oil

Series	Hydrofluorocarbon (HFCs)		Hydrocarbon (HCs)	
Refrigerant	HFO-1234yf	HFC-134a	R1270	R290
Molecular structure				
GWP	4	1410	3	3
Saturated vapor pressure at 298 K (MPa)	0.7	0.7	1.2	1.0
Refrigeration oil	alkyl benzene (AB)		polyalkylene glycol (PAG)	

3. ANTISEIZURE CHARACTERISTICS

3.1 Experimental Apparatus

The experimental apparatus for seizure examination is shown in Figure 1. Disc-on-disc tester was used. The rotated doughnut-shaped test specimen is assembled on the rotated holder. A round fixed test specimen is assembled on the fixed holder. A center position axially of each test specimen is suitable. Both test specimens are separated until examination begins. The load is on the test specimen by a spring in the upper chamber. The load cell is fixed to the upper spring, and the load is measured. Friction force is measured with the load cell installed on the edge of the stopper. Steel ball is installed between the fixed holder and the loading shaft, and the fixed test specimen operated universally, so both test specimens are able to keep parallel. The temperature control pipe was installed in the chamber and atmospheric temperature controlled continuously. The atmospheric temperature is measured with the thermocouple installed in the lower chamber. Regulated refrigerant and refrigeration oil were enclosed in the chamber. The liquid is set at a level higher than the sliding surface. To stir the liquid refrigerant and oil, the stirrer is attached to the rotated holder.

Oil supply procedure to the sliding surface is shown in Figure 2. The oil supply path from the side to lower center is in the fixed holder, and made for the central fixed test specimen. The surface of the rotated test specimen has a radial oil supply groove. When the test specimen rotates, compound refrigerant and refrigeration oil liquid is supplied to the sliding surface through the oil groove.

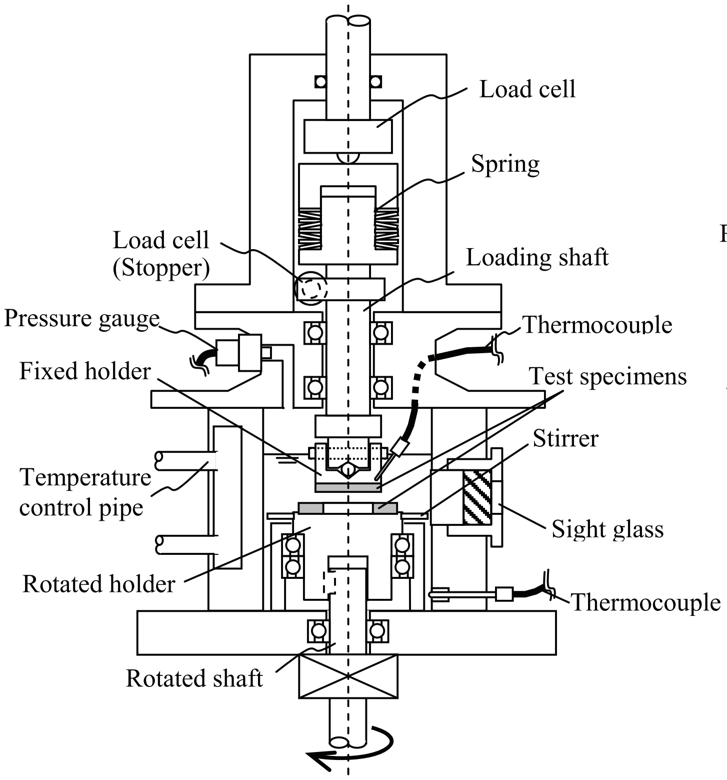


Figure 1: Seizure experimental apparatus

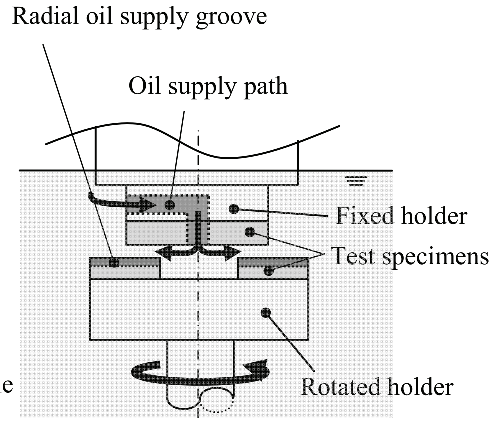


Figure 2: Oil supply procedure

3.2 Experimental Conditions

Seizure experimental conditions are shown in Table 2. Atmospheric temperature was controlled at 298 K. The oil concentration of 50wt% or more is ensured in regular compressor operating conditions, and seizure does not occur in this condition. However, in driving in winter, condensed liquid refrigerant flows to the compressor transiently, and when the compressor starts, seizure may occur. The oil concentration was set at 10 wt%, which is lower than the severest operating conditions in winter. Sliding velocity was previously adjusted to 2.8 m/s and applied load to the test specimen. Figure 3 shows the measurement example of the friction coefficient. The load to test specimens was increased by 100 N minute. As shown in Figure 3, the friction coefficient at steady sliding is 0.04-0.08. It is assumed that seizures occurred when the friction coefficient exceeds 0.15, higher than the stable state. And then the tester stops automatically. The load when the seizure occurred was assumed to be a seizure load. The material of the rotated and the fixed test specimen is cast iron.

Table 2: Seizure experimental conditions

Initial chamber temperature	298 K
Oil concentration	10 wt%
Sliding velocity	2.8 m/s
Incremental load	Stepping 100 N/ min
Data sampling rate	5 s^{-1}
Sliding area	119 mm^2

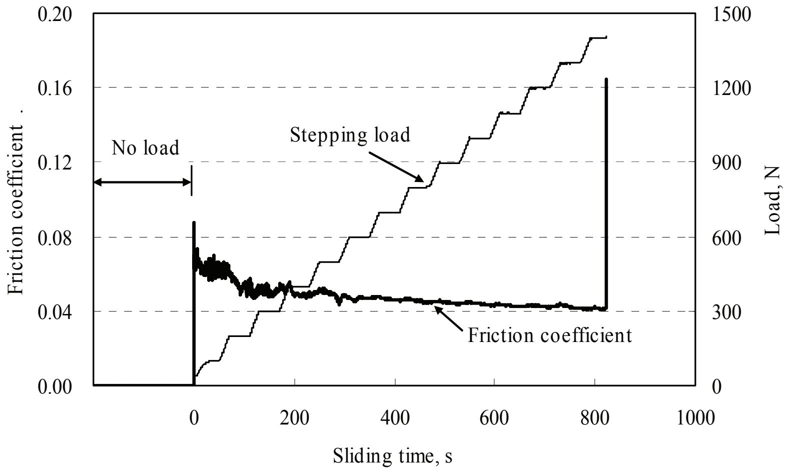


Figure 3: Measurement example of friction coefficient

4. ANTIWEAR CHARACTERISTICS

4.1 Experimental Apparatus

The inside of the chamber in Figure 1 was changed to the pin-on-disc and the wear test done. The experimental apparatus is shown in Figure 4. Three pins were installed in the pin holder. The center of the pin holder agrees with the center of the disc. One sliding line remains on the disc after examination by this structure. Other structures are similar to the seizure tester.

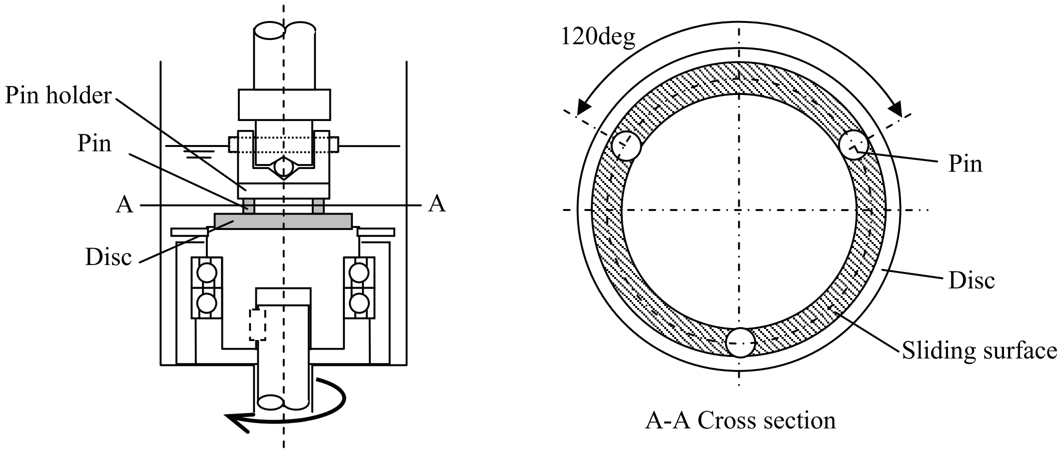


Figure 4: Wear experimental apparatus

4.2 Experimental Conditions

Table 3 shows wear experimental conditions. Regulated refrigerant and refrigeration oil were enclosed in the chamber, and atmospheric temperature was controlled at 298 K. Sliding velocity was previously adjusted to 1.5 m/s and it began to apply the load to the test specimen. Contact pressure was set to 30 MPa, and the wear test done for 48 hours. The material of pin and disc is cast iron.

Table 3: Wear experimental conditions

Initial chamber temperature	298 K
Oil concentration	70 vol%
Sliding velocity	1.5 m/s
Contact pressure	30 MPa
Sliding time	48 h

5. CHEMICAL STABILITY

To clarify chemical stability in the combination of the refrigerant and the refrigeration oil, the amount of sludge generated in liquid while sliding test was evaluated.

5.1 Experimental Apparatus

The experimental apparatus is shown in Figure 5. This tester has a falex examination chamber. Regulated refrigerant and refrigeration oil were enclosed in the chamber. The liquid is set at a level higher than the V block.

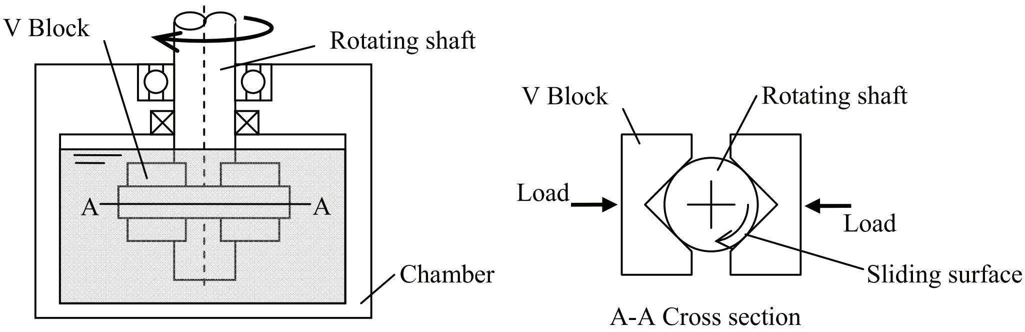


Figure 5: Chemical stability experimental apparatus

5.2 Experimental Conditions

Table 4 shows experimental conditions. The temperature in the chamber is controlled at 448K. After examination for 72 hours, oil in the chamber was collected, filtered, and sludge collected by the filter weighed. The material of the V block is high-speed steel, and that of the shaft is special cast iron.

Table 4: Chemical stability experimental conditions

Temperature	448 K
Refrigerant／Oil	100 ml／350 ml
Test time	72 h
Load	500 N
Revolution	8 s^{-1}

6. EXPERIMENTAL RESULTS

6.1 Antiseizure Characteristics

Seizure load results are shown in Figure 6. The seizure load of HFO-1234yf is larger than that of HFC-134a, and the seizure load of R1270 is larger than that of R290. The unsaturated refrigerant is superior to saturated refrigerant in antiseizure characteristics.

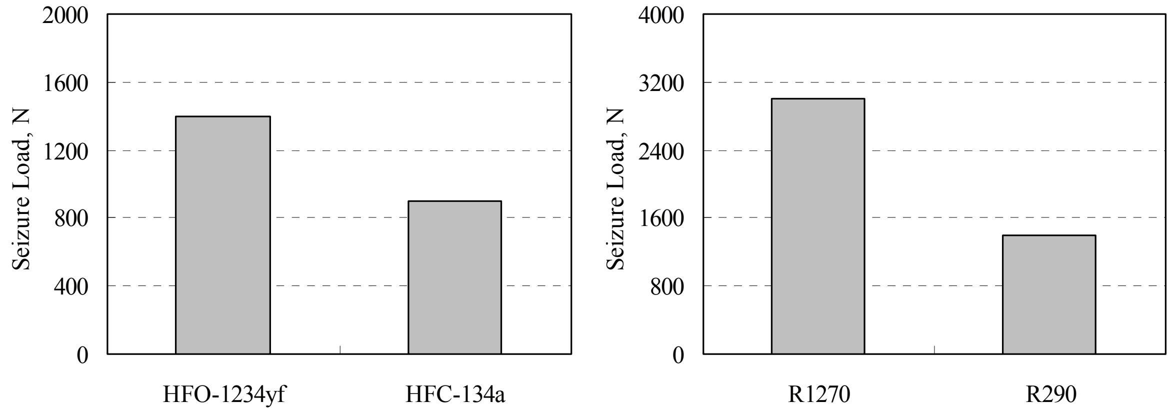


Figure 6: Seizure load

6.2 Antiwear Characteristics

Pin and disc wear depth after sliding tests was measured, and the value in which they were totaled was assumed to be wear depth as shown in Figure 7. The wear depth of HFO-1234yf is less than that of HFC-134a, and that of R1270 less than that of R290, confirming that the unsaturated refrigerant is superior to the saturated refrigerant with antiwear characteristics.

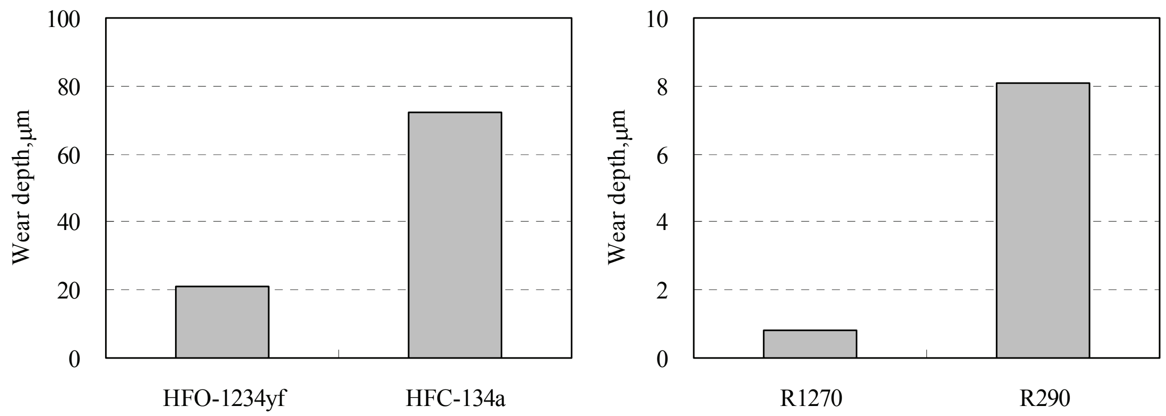


Figure 7: Total wear depth of pin and disc

6.3 Chemical Stability

Figure 8 shows the amount of sludge. That of unsaturated refrigerants was less than that of the saturated refrigerant, so unsaturated refrigerant stability is higher than that of saturated refrigerant. It is known that the amount of the sludge decreases with improved lubrication performance. The amount of the sludge of unsaturated refrigerants was reduced because the refrigerant having the unsaturated bond gives excellent lubrication performance.

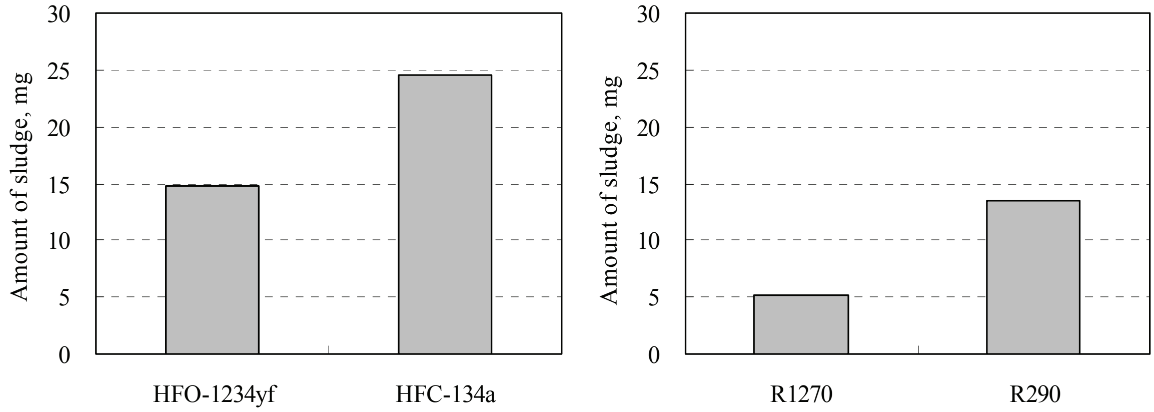


Figure 8: Amount of sludge

7. SURFACE ANALYSIS

To consider lubrication performance of unsaturated refrigerants, the surface of the rotated disc after seizure tests was analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The disc used for analysis was placed into the ultrasonic wave with the acetone after seizure tests to remove excess oil. Figure 9 shows fluorine ion content.

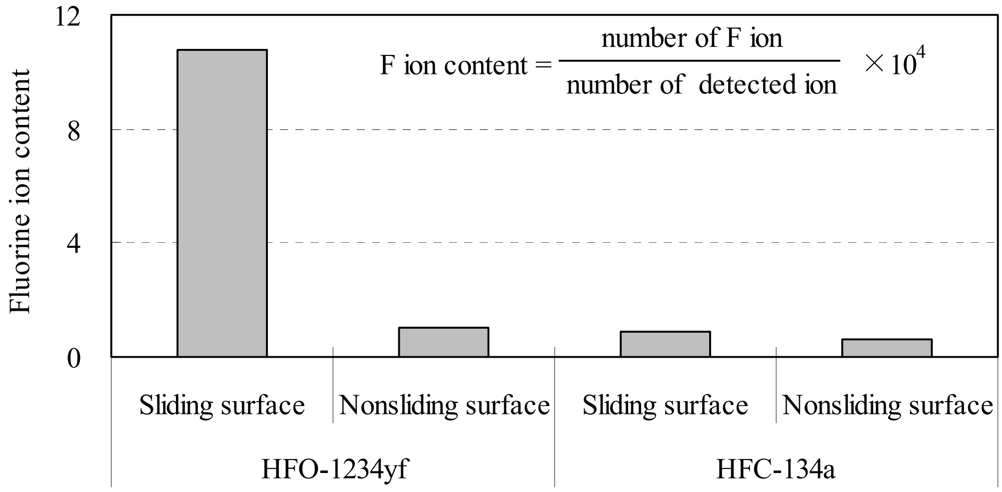


Figure 9: Fluorine ion content measured by TOF-SIMS

As shown in Figure 9, a larger amount of fluorine ions was detected from the sliding surface of the disc examined in the HFO-1234yf atmosphere. Fluorine is a gas at ordinary temperature and pressure, and may have formed fluoride on the disc because of fluorine's high reactiveness. Large differences are observed in the amount of fluorine ions by the sliding surface examined in the HFO-1234yf atmosphere and the other surfaces. For HFO-1234yf with the unsaturated bond, adsorption is strong. It is thought that physisorption film was formed on the test specimen, and this film formed the fluoride layer with frictional heat on the sliding surface. It is difficult in the case of HC refrigerants to presume the influence of the unsaturated bond of the refrigerant on lubrication performance from surface analysis. However, it is surmised that R1270 is superior to R290 in lubrication performance because of a high adsorption of unsaturated bond.

6. CONCLUSIONS

The influence of the unsaturated bond of refrigerants on lubrication performance of the refrigerant was examined. We focused on HFO-1234yf and HFC-134a as HFC refrigerants and R1270 and R290 as HC refrigerants. Lubrication performance of these refrigerants was investigated using immiscible oils. Conclusions are as follows:

- HFO-1234yf, an unsaturated refrigerant, is superior to HFC-134a, a saturated refrigerant, in lubrication performance and reduces sludge.
- R1270, an unsaturated refrigerant, is superior to R290, a saturated refrigerant, in lubrication performance and reduces sludge.
- A large amount of fluorine ions was detected from the sliding surface of the test specimen used in the HFO-1234yf atmosphere. It was thought that lubrication performance of HFO-1234yf was improved by the fluoride layer which was formed with the adsorption effect of the refrigerant and the frictional heat on the sliding surface.
- We surmise that R1270 has excellent lubrication performance due to adsorption by the unsaturated bond.

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