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New Immiscible Refrigeration Lubricant for HFCs

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Abstract

This study examines the application of alkylbenzene (AB), which has been used for many years as a refrigeration oil, to high-pressure dome type rotary compressors for HFCs. By utilizing the low miscibility of AB with HFC refrigerants at high temperatures and pressures, both good lubrication and good oil return performance were achieved at an extremely low viscosity. The results for lubrication performance showed that even low-viscosity AB provided better durability and reliability than conventional mineral oil.

1. Introduction

The primary requirement for the development of refrigeration oils for use with new HFC refrigerants has been the miscibility between the oil and the refrigerant. For this reason, polyol esters (POE) have been chosen for refrigerator applications.

About one-half of all household refrigerators in Japan use rotary compressors. An important issue now is to establish the durability and reliability of rotary compressors for HFC refrigerants because of the severe wear that occurs between the vane tips and rollers in rotary compressors with HFC and POE.

If miscibility could be omitted from the characteristics required of refrigeration oil, then the range of candidates would increase greatly and even include conventional hydrocarbon oils. Mineral oils and alkylbenzene have low miscibility with HFCs, but their moisture absorption is less than one-tenth that of POE and they do not react with moisture. These hydrocarbons are also very stable with HFCs, so they present no risk of copper plating phenomena or other corrosion problems inside refrigeration systems.

This paper presents a study of the possibility of applying AB, which has poor miscibility with HFC refrigerants, to rotary compressors.

2. New AB-type Refrigeration Oils' Physical Characteristics

2.1 Physical Characteristics

2.1.1 Viscosity Characteristics of Low-Viscosity AB

The oil return from the evaporator to the compressor is determined by the viscosity of the oil when the refrigerant is dissolved in the oil and by the surface tension of the oil and refrigerant mixture. Since the return of oil that is poorly soluble with the refrigerant would seem to depend only on the viscosity of the oil itself at low temperatures, we measured the oil's low-temperature viscosity (Table 1). The surface tension of the refrigerant/oil mixture is difficult to measure, but when we measured the surface tension

Table 1 Viscosity of ABs (mm²/s)

Temperature °C	BAB		LAB	POE	Mineral
	VG7	VG22	VG5	VG32	VG56
120	1.55	2.56	1.14	3.53	3.93
100	2.07	3.69	1.44	5.10	6.06
80	2.95	5.83	1.92	8.04	10.5
60	4.59	10.5	2.74	14.3	21.2
40	8.12	22.7	4.30	30.0	54.4
20	17.4	65.4	7.75	80.9	199
0	50.5	294	17.2	316	1270
-10	101	796	28.8	762	4290
-20	237 (430)	2690	53.6	2190 (2100)	19000
-30	637	12000	114	7500	HT 100000
-40	2470 (8600)	78000	292 (390)	35000	HT 100000

(): Measured by Rotary Viscometer, mPa·s

of the oil alone we found no great difference between AB and POE (BAB 29.0, LAB 29.5, POE 29.1 $\times 10^{-3}$ N/m at room temperature).

The viscosity characteristics of linear alkylbenzene (LAB) are better than those of branched alkylbenzene (BAB), and LAB has extremely good flow properties even at low temperatures. In fact, the kinematic viscosity of LAB at -40°C is about the same as that of naphthenic mineral oil ($56 \text{ mm}^2/\text{s}$ at 40°C) at room temperature.

2.1.2 Low-Temperature Viscosity in Presence of Refrigerant

AB is not miscible with large amounts of liquid refrigerant, but gaseous refrigerant dissolves in AB and causes a drop in the kinematic viscosity. We used the testing device shown in Fig. 1 to measure the kinematic viscosity when HFC-134a was dissolved to saturation in BAB at 0 to 20°C , and we compared the results with those obtained for POE. At both 0°C and 20°C , the amount of HFC-134a dissolved in POE increased as the refrigerant pressure increased, making POE advantageous in terms of viscosity. When the refrigerant pressure is low, however, BAB maintains a lower viscosity (Table 2).

2.1.3 Evaluation Test of Oil Return Performance

The testing device shown in Fig. 2 was used to measure the difference in the oil return performance for different oils when the flow rate of the refrigerant gas was held constant at low temperatures. A copper tube 3.6×10^{-3} m in inner diameter was wrapped into a coil and a specified amount of the oil was kept inside the tube at a fixed temperature while HFC-134a was passed through the tube at the rate of $0.001 \text{ m}^3/\text{min}$. The oil/refrigerant mixture was recovered at the tube outlet. After the refrigerant was removed, the remaining oil's weight was measured to determine the oil return rate.

The oil return rate was better for low-viscosity AB at -20°C and higher, while POE had a better oil return rate at -30°C and below. When the temperature was above the boiling point of the refrigerant, the refrigerant/oil mixture was returned in separate gas and liquid phases, so the AB with low viscosity at low temperatures was superior. Because HFC-134a became a liquid when the temperature inside the tube was below the refrigerant's boiling point, POE returned in the same liquid phase with the refrigerant since POE is intended to be miscible with the liquid refrigerant; AB, in contrast, returned in two separate liquid phases. Thus the oil return is better for POE, but the oil return performance of LAB is nearly as good as that of POE because LAB maintains its low viscosity even at low temperatures. (Table 3, Figs 2,3,4)

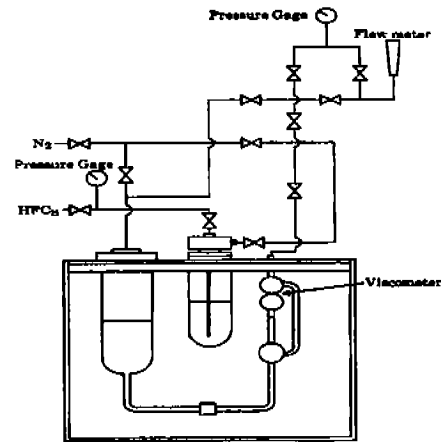


Fig.1 Testing Device for Solubility of Refrigerants into Oils

Table 2 Solubility of HFC-134a at Low Temperature

Temperature $^{\circ}\text{C}$	Pressure MPa	Oil	Solubility of HFC-134a mass %	Kinematic Viscosity mm^2/s
0	0.20	BAB7	9.82	24.9
		POE	21.5	33.4
20	0.20	BAB7	5.64	12.9
		POE	10.1	31.6
20	0.29	BAB7	5.69	11.6
		POE	16.6	18.6

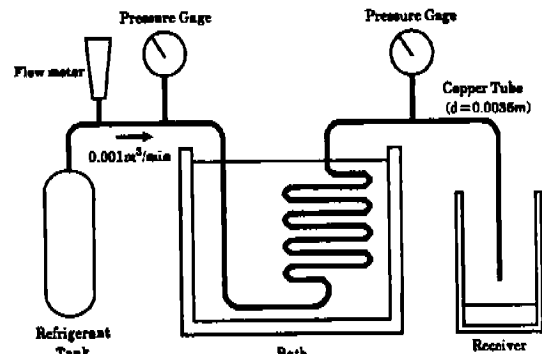


Fig.2 Testing Device for Oil Return Property

Table 3 Oil Return Rate (mass %)

Temperature $^{\circ}\text{C}$	BAB		LAB	POE
	VG7	VG22	VG5	VG32
-40	10.4	2.6	63.8	98.7
-30	45.3	7.2	97.3	98.4
-20	31.2	2.4	38.5	31.1
-10	33.9	9.4	46.7	30.2
0	42.4	21.0	49.3	24.0

Gas Flow Rate: $0.001 \text{ m}^3/\text{min}$, Test Period: 30min

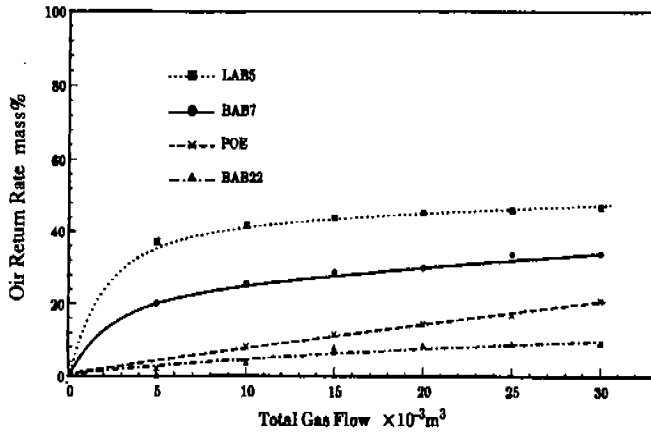


Fig.3 Oil Return Property at -10°C

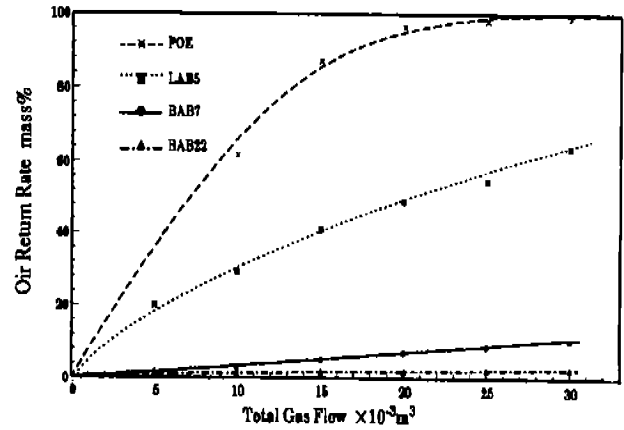


Fig.4 Oil Return Property at -40°C

2.1.4 Solubility of Gaseous Refrigerant at High Temperatures

The device shown in Fig. 1 was also used to measure the saturation solubility and kinematic viscosity of HFC-134a gas in each type of oil under high temperature and pressure in order to confirm the behavior of the oil and refrigerant inside the compressor. HFC-134a was well soluble with POE even at high temperatures, while little HFC-134a dissolved in AB; in fact, the amount was only about 50 mass% of that in POE under the same conditions (Table 4). In high-pressure dome type rotary compressors, the dissolution of the refrigerant gas in the oil can cause the pressure to drop. Therefore oils such as AB that are immiscible in HFCs can be expected to prevent the drop in cooling efficiency caused by the dissolution of the refrigerant in the oil and thus make it possible to reduce the amount of refrigerant.

2.1.5 Miscibility of Liquid Refrigerant at High Temperatures

We observed visually the solubility of the oil in the liquid refrigerant at high temperatures in order to confirm the behavior inside the condenser. A specific amount of oil colored with "Liquid Red" was placed into a pressure-resistant glass tube and enough HFC-134a was added to reach a specific concentration. Varying the temperature of the liquid in the water bath, we observed the degree of dissolution of the oil at each temperature (Table 5). Low-viscosity BAB was miscible with HFC-134a at a condenser liquid temperature around 50 or 60°C, up to an oil concentration of about 3 mass%. The miscibility of low-viscosity LAB was slightly inferior to that of BAB, although we did confirm miscibility up to about 2.5 mass%.

Table 4 Solubility of HFC-134a at High Temperature

Temperature °C	Pressure MPa	Oil	Solubility of HFC-134a mass %	Kinematic Viscosity mm ² /s
80	0.69	BAB7	2.62	2.32
		POE	6.53	5.27
80	0.88	BAB7	4.13	2.08
		POE	8.69	4.73
60	0.49	BAB7	4.93	3.60
		POE	8.65	8.13

Table 5 Miscibility of AB into HFC-134a Liquid

Conc. mass %	Oil	Temperature °C												
		0	5	10	15	20	25	30	35	40	45	50	55	60
0.5	BAB 7	M	M	M	M	M	M	M	M	M	M	M	M	M
	LAB 5	I	I	P	M	M	M	M	M	M	M	M	M	M
	BAB 22	I	I	I	I	I	I	I	I	I	I	I	I	I
1.0	BAB 7	P	M	M	M	M	M	M	M	M	M	M	M	M
	LAB 5	I	I	P	M	M	M	M	M	M	M	M	M	M
	BAB 22	I	I	I	I	I	I	I	I	I	I	I	I	I
1.5	BAB 7	I	P	M	M	M	M	M	M	M	M	M	M	M
	LAB 5	I	I	I	I	P	M	M	M	M	M	M	M	M
	BAB 22	I	I	I	I	I	I	I	I	I	I	I	I	I
2.0	BAB 7	I	I	P	P	M	M	M	M	M	M	M	M	M
	LAB 5	I	I	I	I	I	I	I	P	M	M	M	M	M
	BAB 22	I	I	I	I	I	I	I	I	I	I	I	I	I
2.5	BAB 7	I	I	I	I	I	I	I	P	M	M	M	M	M
	LAB 5	I	I	I	I	I	I	I	I	P	P	P	P	P
	BAB 22	I	I	I	I	I	I	I	I	I	I	I	I	I
3.0	BAB 7	I	I	I	I	I	I	I	I	I	I	P	P	P
	LAB 5	I	I	I	I	I	I	I	I	I	I	I	I	I
	BAB 22	I	I	I	I	I	I	I	I	I	I	I	I	I

M: Miscible, P: Partially miscible, I: Immiscible

2.2 Chemical Stability and the Effect of Impurities

An important problem that must be solved for HFC-134a refrigerators is the sludge precipitation in the capillaries. There are two main types of precipitates that have been found in systems using POE. One type is wax and other solids that are insoluble in HFC-134a, while the other type is metallic soaps that form due to the hydrolytic degradation of POE and the additives. Table 6 shows the solubility of paraffin wax in oil and refrigerants.

The mechanism of capillary sludge formation is believed to be as follows. While both AB and POE dissolve impurities such as wax inside the compressor, when the oil containing such impurities is discharged into the refrigeration cycle in the presence of large amounts of refrigerant, POE, which is very miscible with the refrigerant, dissolves into the liquid refrigerant. The solid and semisolid impurities which are rejected by the refrigerant therefore collect around the capillary outlet, which has the lowest temperature in the fluid line. While both AB and POE dissolve the impurities, AB can dissolve a large amount of solids and does not allow the solids to precipitate because AB is not miscible with HFC-134a at low temperatures.

The sliding environment in rotary compressors is particularly severe, and metallic soaps have been known to form as a result of wear when POE is used. Those soaps then precipitate in the capillaries. Even very stable POE made from α -branched fatty acids has undergone hydrolysis and formed sludge during long-term sealed tube tests in the presence of water at 175°C. In contrast, AB undergoes no change at all whether or not additives or moisture are present (Table 7). Thus AB is extremely effective for preventing the contamination of capillaries.

2.3 Lubrication Characteristics

Although there is little viscosity decrease caused by the mixture with the HFC refrigerant in the refrigerant environment, from the point of view of oil performance it is necessary to use AB with as low a viscosity as possible. Therefore we evaluated the lubrication characteristics of low-viscosity AB in HFC refrigerant.

2.3.1 Falex Test

The seizure load of AB alone is about 1.78 kN when HFC-134a is blown at the test piece. However, this load can be improved to about 3.10 kN by blending the AB with antiwear agents that have been used in current refrigeration oils. The amount of pin wear in the wear test of low-viscosity BAB containing antiwear agents was about 13 mg, which was about the same amount as with naphthenic mineral oil in the presence of CFC-12. This was more wear than with POE, however (Table 8).

Table 6 Comparison of Solubility of Wax (°C)

Concentration of Wax ppm	50	100	250	500	1000	5000
AB (BAB) VG22	<-20	<-20	<-20	<-20	<-20	+15
with 80 wt% HFC-134a Liquid	<-20	<-20	<-20	<-20	<-20	+15
Mineral VG22	<-20	<-20	<-20	<-20	<-20	+15
with 80 wt% HFC-134a Liquid	<-20	<-20	<-20	<-20	<-20	+15
POE VG22	<-20	<-20	-5	0	+15	-
with 80 wt% HFC-134a Liquid	0	+5	+20	+25	>+35	-
PAG VG22	<-20	-10	5	+15	+20	-
with 80 wt% HFC-134a Liquid	0	+5	+20	+30	>+35	-

Table 7 Sealed Tube Test Results

Base Oil	Temperature °C	Moisture ppm	Results (60 days)	
			Color	Sludge
BAB7	175	500	L0.5	None
POE	175	500	Milky	Found

Catalyst: Steel, Copper, Aluminum (wire)

Table 8 Falex Test Results

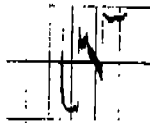
Oil	Additives (Antiwear)	Refrigerants	Seizure Test	Wear Test
			Load at Failure kN	Wear to Pin mg
BAB7	None	HFC-134a	1.78	Failed
	Phosphate	HFC-134a	2.89	13.8
BAB22	None	HFC-134a	1.86	Failed
	Phosphate	HFC-134a	3.10	13.0
POE	None	HFC-134a	5.55	1.1
	Phosphate	HFC-134a	5.77	0.5
Mineral	None	CFC-12	2.66	13.1

Wear Test Conditions: Load: 1.11kN, Temperature: 80°C, Test Period: 1hr

2.3.2 Friction Test in High-Pressure Environment

Using the test method shown in our other report¹⁾, we observed the contact conditions by passing electrical current through the test pieces. In the disk-disk test, there was no significant difference between the contact conditions with AB and POE. In the vane-disk test, however, AB showed superior results. When used alone, AB was similar to POE in that once metal contact occurred and the electrical circuit was completed, it was impossible to return to hydrodynamic or mixed lubrication. When even a small quantity of antiwear agents was added, however, the same amount of break-in smoothing occurred as in the case of CFC-12, and it was possible to avoid metal contact even at fairly high loads. This phenomenon was the same regardless of the viscosity of the AB. While conventional additives had not had sufficient effect when used in small amounts with POE, it was clear that, when AB is used, such additives are effective with HFC refrigerant applications (Figs. 5,6).

BAB 7 (HFC-134a)

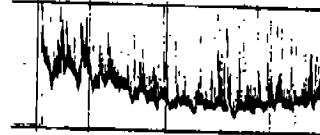


BAB 7+phosphete



BAB 7+phosphete 1/6

4.41 kN



BAB 22+phosphete



4.41 kN

POE (HFC-134a)



Mineral (CFC-12)



1.18 kN

1.18 kN

Fig.5 Electrical Current at the Disk and Disk

Fig.6 Electrical Current at the Vane and Disk

3. Rotary Compressor Durability Tests

We ran a short-term durability test using a horizontal rotary compressor of the type used in actual refrigerators. The compressor was a model currently used with CFC-12. We ran a short-cycle test in which the discharged gas was extracted with a needle valve and returned directly to the system inlet. The test conditions are shown below.

- Refrigerant: HFC-134a
- Quantity of oil: 130 g
- Discharge pressure: 2.94 MPa
- Discharge temperature: 110°C
- Inlet pressure: 0.157 MPa
- Frequency: 50 Hz
- Test time: 2,000 hr

As shown in Table 9, the AB/HFC-134a combination showed superior wear prevention to the naphthenic oil/CFC-12 combination in the 1,000 hr evaluation, regardless of the viscosity of the base oil. Low-viscosity AB without antiwear

additives was also evaluated; although poor lubrication was observed on some parts of the shaft, there was no significant wear between the vanes and rollers. With AB/HFC combinations, it is necessary to take into consideration not only the chemical reaction of the antiwear agents on the metal surfaces but also the rheological behavior of the AB.

Table 9 Compressor Test Results

Oils	Additives	Refrigerant	Wear at Sliding Parts	
			Vane / Roller	Shaft / Bearing
BAB7	None	HFC-134a	Good	Fair
	Phosphate	HFC-134a	Good	Good
LAB5	None	HFC-134a	Good	Fair
	Phosphate	HFC-134a	Good	Good
POE	Phosphate	HFC-134a	Mild	Good
Mineral	None	CFC-12	Slight	Good

4. Conclusion

We have developed AB oils with extremely low viscosities for use as refrigeration oils with HFC refrigerants. The development of these oils started with the goal of sacrificing the miscibility with the refrigerant, but as a consequence it became possible to drastically lower the oil's viscosity and to ensure good oil return performance at low temperatures. These oils' antiwear characteristics in rotary compressors are better than those of conventional mineral oils, and they cause no sludge precipitation problems of the type observed with POE oils. Since these new AB oils do not dissolve HFCs that become mixed with the oil in high-pressure compressor chambers, it is also possible to reduce the amount of refrigerant in the new refrigeration system.

5. Reference

- 1) M. Sunami, K. Takigawa, S. Suda, "Optimization of POE Type Refrigeration Lubricants," ASHRAE-Purdue CFC Conference, July 1994