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Optimization of POE Type Refrigeration Lubricants

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Abstract

The optimization of POE was studied for use in rolling piston type rotary compressors. Antiwear agents that would improve the wear resistance between the vanes and rollers were sought, and a new stabilizer was successfully developed for improving the hydrolytic stability, which is an important problem for both POE and antiwear agents. The newly developed stabilizer both maximizes the antiwear effect of the antiwear agents in the POE and makes it possible to hold down the increase in the total acid number. Thus a POE-type refrigeration lubricant has been developed which ensures long-term stability.

1. Introduction

The compressors of household refrigerators are the hermetic type with internal motors. Because the electrical connectors are immersed in a mixture of refrigeration oil and refrigerant, POE has been adopted as the refrigeration oil because of its good electrical insulation properties and good miscibility with HFCs. POE has already been applied commercially in reciprocating compressors. However, when POE has been used in rotary compressors, heavy wear has been observed between the vane tips and the rollers. It is difficult to ensure sufficient wear resistance with currently used sliding materials, so research and development are focusing on ensuring adequate durability and reliability. In Japan, nearly all room air conditioners use rotary compressors, and the biggest challenge facing us today is overcoming the wear problem when HFC refrigerants are adopted as substitutes for CFCs and HCFCs.

HFC refrigerants are unlike CFCs in that HFCs contain no chlorine atoms, which act to reduce extreme-pressure effects. Therefore greater wear prevention is required of the refrigeration oil. This need must be met not only in the molecular design of the POE but also in the development of additive technology.

2. Development Issues for Refrigeration Oils for HFC Refrigerants

2.1 Solubility and Miscibility with Refrigerant

Table 1 shows the miscibility relationship between the POE structure and HFC refrigerants. In the present study, we compared the two-phase separation temperature of POE. The alcohols used to make the POE were hindered polyols, which have advantages in terms of stability. The fatty acids used were monobasic acids with 5 to 9 carbons. In general, the POEs made from linear fatty acids were poorly miscible with the HFC refrigerants. In the case of the PE-type POEs, HFC-134a and the linear fatty acid esters with 8 or more carbons separated into two layers even at room temperature. In order to obtain miscibility with HFC refrigerants, the POE structure must include at least a certain amount of branched fatty acids.

Table 1 Physical Properties of POEs

Name	Poly -ol	Organic Fatty Acids							Kinematic Viscosity	Phase Separation
		C5	C6	C7		C8		C9		
		L	L	L	B	L	B	B	mm^2/s @40°C	°C @10 mass%
TH7L	TMP			X					13.6	-24
TH8B					X				24.6	-31
H5L	PE	X							15.8	LT -70
H6L			X						18.2	-50
H7L				X					21.9	-4
H8L						X			28.5	HT R.T.
H7B	PE				X				26.6	-48
H8B							X		45.3	-21
H9B								X	110	-28
H7B8B	PE				X		X		30.2	-43
H8B9B							X	X	66.3	-24
H5L9B	PE	X						X	73.2	-41
H7L9B				X				X	65.4	-24
H8L9B						X		X	55.2	+2

HFC blends have been studied as substitutes for HCFC-22. A leading candidate is HFC-32/125/134a (with a typical composition of 23/25/52 mass%). In this case, the low miscibility of HFC-32 cancels out the high miscibility of HFC-125, so the blend has nearly the same miscibility as HFC-134a alone(Table 2). R404A has begun to be used as a substitute for R502, demonstrating excellent miscibility with POE despite the low miscibility of HFC-143a, which is the main component of R404A. It is hoped R404A will offer better oil-return performance at low temperatures than the current mineral oil and R502 combination.

Fig. 1 and 2 show the viscosity changes caused by the solubility between POE and the refrigerant gas. The solubility of HFC-134a in POE is less than the solubility of CFC-12 in naphthenic mineral oil. The viscosity of the POE/HFC-134a mixture is higher than that of the mineral/CFC-12 mixture under the same conditions. The HFC blend (HFC-32/125/134a) tends to lower the viscosity of POE more easily than does HFC-134a by itself, and the viscosity decrease is particularly strong at high temperatures. Because rotary compressors experience high temperatures and pressures inside their containers, it is particularly important to select a POE that has sufficient viscosity characteristics to maintain a hydrodynamic oil film.

2.2 Optimization of Lubricity

When the durability of rotary compressors is evaluated with POE, severe wear occurs in some cases between the vanes and rollers. This wear can be reduced if conventional phosphate ester antiwear agents are used, but the level of wear is still unacceptable. Because of the strict limitations imposed by the stability, miscibility, and other factors related to the compatibility with the refrigerant, this optimization study focused on phosphate esters as the antiwear agents.

2.2.1 Falex Wear Test

The refrigerant (HFC-134a) was blown into the tester from directly below the specimen (at a rate of 0.01 m³/h). After 5 minutes of break-in operation, the test was run for 1 hour at 100 °C and 1.11 kN. When the test was finished, the amount of wear to the pin was measured. The amount of dissolved refrigerant in this case was approximately 1.5 mass%. The results are shown in Table 3.

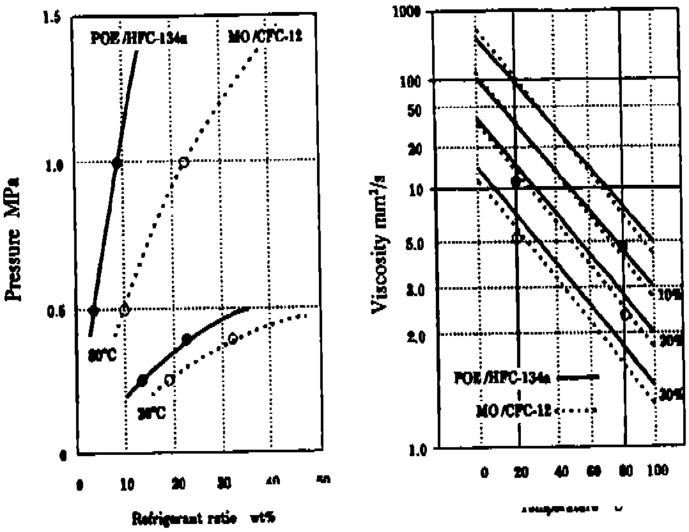


Fig 1 Solubility of Refrigerants (Comparison of POE/HFC-134a and MO/CFC-12)

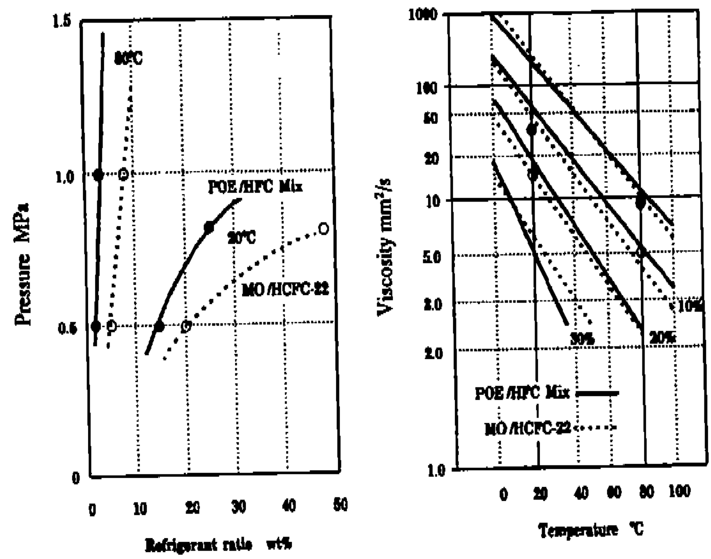


Fig 2 Solubility of Refrigerants (Comparison of POE/HFC Mix* and MO/HCFC-22)
*HFC Mix : HFC-32/125/134a = 23/25/52 wt%

Table 2 Miscibility of HFCs with POEs

HFCs	Phase Separation °C @10 oil mass%		
	H7B8B (VG32)	H8B9B (VG68)	PAG (VG32)
32	-2	+20	-30
125	LT -70	LT -70	LT -70
134a	-43	-24	LT -70
143a	+50	HT+50	HT+50
152a	LT -70	LT -70	LT -70
Mixed*	-43	-23	LT -70
R404A	LT -70	LT -70	LT -70

*Mixed: HFC-32/125/134a = 23/25/52 wt%

Table 3 Falex Wear Test of POEs

L		LB		B	
Type	Wear to Pin mg	Type	Wear to Pin mg	Type	Wear to Pin mg
TH7L	23.7			TH8B	13.3
H5L	17.1	H5L9B	6.5	H7B8B	1.1
H6L	0.5	H7L9B	6.6	H8B	0.8
H7L	0.4	H8L9B	2.5	H8B9B	3.2

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

Table 4 Falex Wear Test of POEs with Additives

POE	Additives (Antiwear)	Additives (Stabilizer)	Refrigerant	Wear to Pin mg
H8B9B	None	None	HFC-134a	3.2
H8B9B	PA	None	HFC-134a	2.4
	PB	None	HFC-134a	2.2
	PC	None	HFC-134a	1.9
H8B9B	PC	AA	HFC-134a	1.9
	PC	AB	HFC-134a	2.5
	PC	AC	HFC-134a	2.4
Mineral	None	None	CFC-12	13.1

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

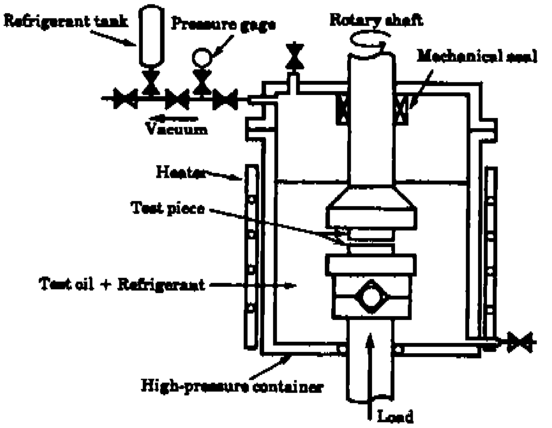
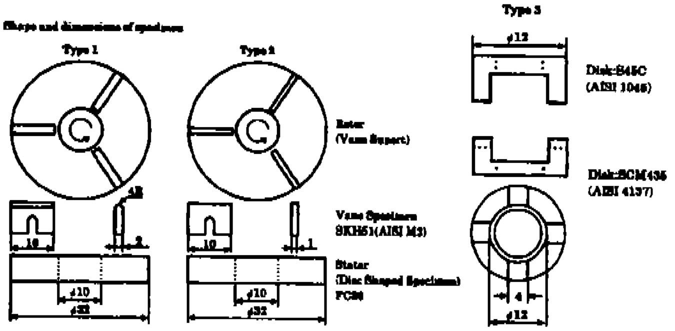


Fig. 3 Friction Test Machine under High Pressure of Refrigerants



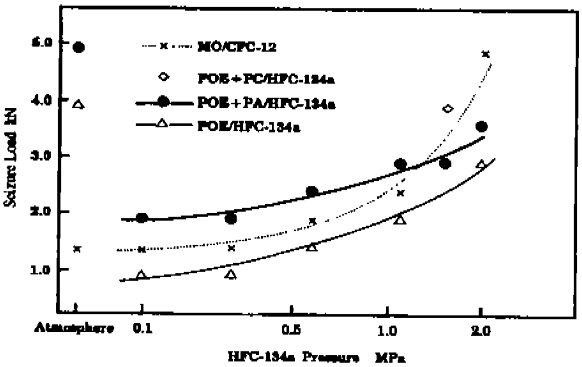


Fig. 4 Disk/Disk Seizure Test under High Pressure of Refrigerants

Table 5 Vane-Disk Test of POEs

POE	Additives (Antiwear)	Refrigerant	Wear to Disk mg
H7B8B	None	HFC-134a	6.2
	PA	HFC-134a	3.3
	PB	HFC-134a	0.9
	PC	HFC-134a	0.4
Mineral	None	CFC-12	1.1

Load: 2.45kN, Refrigerant Pressure: 1.57MPa
Temperature: 80°C, Test Period: 6hrs

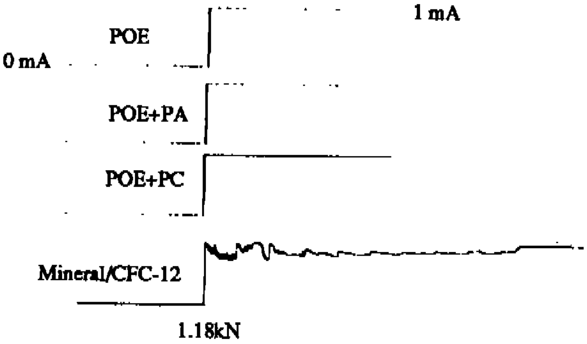


Fig. 5 Electrical Current at the Vane and Disk

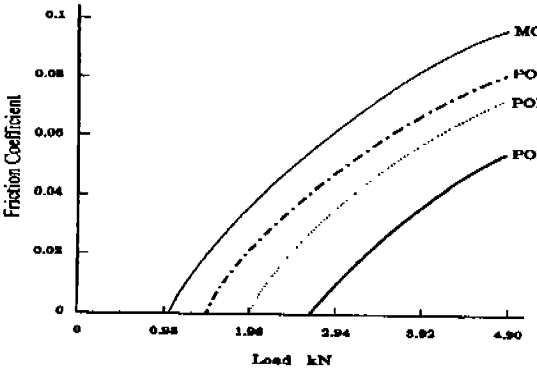


Fig. 6 Friction Coefficient in the Vane/Disk Test

The wear characteristics of POE in the Falex test are determined by the chemical structure. It was found that POE consisting only of linear fatty acids with longer chains performed better than POE that contained branched fatty acids. The wear characteristics also varied depending on the structure of the branched chains. The results showed that POE consisting solely of branched fatty acids had better wear prevention characteristics than POE that contained some linear fatty acids.

2.2.2 Wear Test in High-Pressure Environment [1)]

In order to create test conditions close to those in actual use, we obtained a testing device that could maintain the testing section in a high-temperature, high-pressure refrigerant environment (Fig. 3). Our wear tests were run on this device.

(1) Seizure Test (Disk-Disk Test)

Two disks were rotated against each other at 500 rpm, with the load increased by 0.49 kN every 10 minutes. (The stationary test disk had an oil feed groove.) The load at which the friction coefficient increased sharply was regarded as the seizure load. The test was run at an oil temperature of 80°C and a speed of 500 rpm.

(2) Wear Test (Vane-Disk Test)

We ran a wear test in which three vanes of the type shown in Fig. 3 were rotated on a disk at a load of 2.45 kN for 6 hours. When the test was finished, we measured the wear to the disk. The test was run with an oil temperature of 80°C, a refrigerant pressure of 1.57 MPa, and a rotation speed of 500 rpm.

(3) Observation of Contact Conditions by Passing Electricity Between the Test Pieces

In the disk-disk test and vane-disk test, electrical current was passed between the upper and lower test pieces to observe the contact conditions between the pieces as the load was gradually increased. In the disk-disk test, the load was increased by 0.098 kN every 2 minutes. In the vane-disk test, the load was increased by 0.245 kN every 2 minutes. The oil temperature was 80°C and the refrigerant pressure was 1.57 MPa. In the vane-disk test, the surfaces of the vanes were rounded so that the contact condition would be close to that in actual compressors.

Although the seizure load of POE in air is extremely high, the seizure load decreases sharply once the test piece is placed in an environment containing the refrigerant. As the amount of refrigerant is increased, the seizure load increases with both CFC-12 and HFC-134a, presumably because of the cooling effect of the refrigerant on the sliding surfaces. In the case of CFC-12, the sharp increase in the seizure load and the decrease in wear that accompanied the increase in the amount of refrigerant were due to the antiwear effect of the chlorine contained in this refrigerant. In the cases of POE and HFC-134a, the effect of phosphate ester A (PA) decreased as the refrigerant pressure increased, presumably because of the dilution of the additive by the refrigerant and the significant decrease in the physical adsorption of the additive to the steel surface caused by the refrigerant's polarity. The additive PC, which is more active than PA, exhibited a high seizure load even under high refrigerant pressure, indicating that it would be effective in a POE/HFC combination.

Table 6 Hydrolytic Stability Test of POEs

POE	Additives	Temperature ℃	Atmosphere	Moisture ppm	TAN mgKOH/g	
					7 days	14 days
H7L	None	150	N_2	1000	0.20	1.9
H5L9B	None	150	N_2	1000	0.10	1.3
	None	175	N_2	1000	4.4	5.0
	None	175	HFC-134a	1000	-	0.18
H7B8B	None	150	N_2	1000	0.01	0.02
	None	175	N_2	1000	0.05	0.17
	None	175	HFC-134a	1000	0.01	0.02
H8B9B	None	150	N_2	1000	0.01	0.02

Catalyst: Steel, Copper, Aluminum (wire)

POE maintained an oil film in HFC refrigerant at low loads. As the load increased to a critical level, however, the oil film would break, resulting in either mixed lubrication or boundary lubrication. The rate of electrical connection increased in the disk-disk test as the load increased, resulting eventually in a perfect electrical connection. The critical load was about the same (around 1.18 kN) for both POE and mineral oil regardless of whether antiwear agents were present. The antiwear agents are effective against break-in smoothing after the start of metal contact, indicating the effect of these agents with POE as well.

In the vane-disk test as well, the oil film was completely maintained at the start of the test, and the critical load was around 1.18 kN regardless of the type of oil or refrigerant. As in the disk-disk test, the start of break-in smoothing led to mixed lubrication with naphthenic mineral oil/CFC-12; with POE/HFC-134a, however, it was impossible to avoid boundary lubrication after the start of metal contact regardless of how active the antiwear agents were. However, the friction coefficient was lower when an antiwear agent with higher activity was used, confirming the effectiveness of such additives.

From the above results, we can conclude that wear is likely to occur along the contact lines between the vanes and rollers in the case of POE/HFC. To prevent this wear, it is necessary to select highly active additives that can adsorb to the steel surface both physically and chemically even in the presence of polar substances such as POE and HFC.

3. The Stability of POE

The formation of fatty acids by the hydrolysis of POE can result in the formation of ferrous soaps due to corrosion as well as in an increase in the total acid number (TAN) and many other problems. Therefore, when an oil is to be used in rotary compressors where it will be exposed to high temperatures and pressures, it must have good hydrolytic stability. The saturation solubility of moisture in POE is about 1,000 ppm at room temperature. Therefore we evaluated the hydrolytic stability of POE by adding 1,000 ppm of water in the presence of either the refrigerant or nitrogen. The experiment in the refrigerant environment was conducted inside an autoclave using HFC-134a at two temperature levels, 150°C and 175°C. The experiment in the nitrogen environment was conducted in a glass container at 150°C. In the test in the refrigerant environment, the added water hydrated to the refrigerant and shifted to the gas phase, so the rate of hydrolytic stabilization was slower than in the nitrogen environment.

The hydrolysis of POE is determined by the molecular structure of the fatty acid. Branched fatty acids with steric hindrances are more stable than linear fatty acids, and POE containing α-branched fatty acids that can block the attack of the moisture on the carbonyl groups is extremely stable against hydrolysis (Table 6). However, when phosphate esters are used as antiwear agents, the decomposition of the additives occurs first. Some of the PA has decomposed into acidic phosphate ester, and the quantity of the phosphorus found by ^{31}P-NMR matches closely the increase in the TAN. This seems to be due to excessive hydrolysis of the phosphate esters away from the sliding parts. Therefore, when developing oils for rotary compressors, we must ensure the stability not only of the base oil POE but also of the additives.

When the same phosphate ester and epoxide type stabilizers were added to PAG and POE, there was very little increase in the TAN of the PAG oil, indicating that the moisture behaves differently from the case of POE (Table 7).

The highly active phosphate esters consume the moisture in POE quickly and cause the sharp increase in

Table 7 Comparison of Hydrolysis of POE and PAG

Base Oil	Additives	Temperature ℃	Atmosphere	Moisture ppm	TAN mgKOH/g	
					7 days	14 days
H7B8B	None	150	N_2	1000	0.01	0.02
	PA	150	N_2	1000	1.3	2.1
	PA	175	HFC-134a	1000	0.10	1.4
PAG	None	150	N_2	1000	0.01	0.01
	PA	150	N_2	10000	0.04	-
	PA	150	N_2	10000	0.04	-
	PA	175	N_2	1000	0.01	-
	PA	175	N_2	10000	0.16	-

Catalyst: Steel, Copper, Aluminum (wire)

Table 8 Improvement of Hydrolytic Stability of POEs

POE	Additives Antiwear	Additives Stabilizer	7 Days		14 Days	
			TAN mgKOH/g	Moisture ppm	TAN mgKOH/g	Moisture ppm
H8B9B	None	None	0.01	1000	0.02	990
H8B9B	PA	None	1.6	280	3.0	120
	PB	None	4.7	300	5.6	220
	PC	None	4.6	300	5.4	170
H8B9B	PA	AA	1.5	200	1.9	150
	PA	AB	0.82	260	1.8	110
	PA	AC	0.01	1020	0.01	980
	PC	AA	2.2	140	2.9	100
H8B9B	PB	AC	1.1	190	1.9	140
	PC	AC	0.02	1000	0.07	880
H5L9B	None	None	0.10	920	1.3	600
	PC	None	5.7	140	4.8	120
	PC	AC	0.04	1000	0.73	840

Initial Moisture: 1000ppm, Catalyst: Steel, Copper, Aluminum (wire) the TAN. However, we have confirmed that the stabilizer we developed behaves similarly to PAG by preventing the moisture in the system from contributing to hydrolysis. Almost no change in the amount of moisture was observed between before and after the experiment, and the stabilizer had extremely high stability even when compared with epoxide additives that have been used as acid scavengers.

When only stabilizer C was added to the POE base oil, this stabilizer had less effect than with the phosphate esters, perhaps because stabilizer C stays near the phosphate esters in the oil and so prevents the reaction with the moisture. However, the actual mechanism is unknown at present.

4. Rotary Compressor Durability Tests

We ran a short-term durability test using a horizontal rotary compressor of the type used in actual refrigerators in order to confirm the additive effect of antiwear agents and stabilizers. The compressor was a type currently used with CFC-12 (cylinder volume 4.3 X 10^{-6} m^3). 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
Discharge pressure: 2.94 MPa
Discharge temperature: 110°C
Inlet pressure: 0.157 MPa
Frequency: 50 Hz
Test time: 1,000 hr

As shown in Table 9, abrasive wear was observed when POE was used alone under the same conditions as naphthenic mineral oil and CFC-12. When the antiwear agent PB was added, however, the results were nearly the same. When this durability test was run with only stabilizers added to the POE, the results were better than with POE alone. These results confirm those already reported 2),3)and demonstrate the reliability of our experiments.

Table 9 Compressor Test Results

POE	Additives (Antiwear)	Additives (Stabilizer)	Refrigerant	Wear at Sliding Parts	
				Vane/Roller	Shaft/Bearing
H8B9B	None	None	HFC-134a	Severe	Fair
H8B9B	None	AA	HFC-134a	Fair	Good
H8B9B	PA	AA	HFC-134a	Mild	Good
H8B9B	PC	AC	HFC-134a	Slight	Good
H8B9B	PC	None	HFC-134a	Slight	Good
Mineral	None	None	CFC-12	Slight	Good

5. Conclusion

The antiwear agents used with POE in HFC refrigerant rotary compressors must be chosen to match the compressors' characteristics. It is important to control the hydrolytic degradation of the POE base oil and antiwear agents at locations other than the sliding surfaces. By using POE base oil with a branched fatty acid structure together with antiwear agents and stabilizers, we were able to optimize the lubricant performance.

Refrigeration oils are used for long periods of time without being replaced, so it is very important to ensure the oils' stability. We plan to continue to improve the long-term reliability of these oils by optimizing the oils in conjunction with the sliding materials.

6.References

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