Purdue University
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International Refrigeration and Air Conditioning Conference

School of Mechanical Engineering

2012

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ABSTRACT

R410A, which has a high GWP (global warming potential) of roughly 2000, is widely used in refrigeration systems today. Various low GWP alternative refrigerants have been investigated as part of the effort to stop global warming. One such refrigerant, R32, offers an alternative that improves system performance without the need for significant changes to current systems. Moreover, its GWP is roughly 1/3 that of R410A. R32 is thus a very promising candidate to replace R410A. However, current refrigeration oils designed for use with R410A have poor miscibility with R32. In this paper, we report on solutions to the miscibility problem and the characteristics of refrigeration oils for R32 systems.

1. INTRODUCTION

The impact on global warming of refrigerants leaking into the atmosphere becomes greater by the year. This has spurred studies to look for low GWP alternatives. In the field of car air conditioners, the F-GAS regulations were adopted in Europe with the result that R134a is now subject to regulation because its GWP (1300) exceeds the threshold set at 150. Consequently, the refrigerant HFO-1234yf, with a GWP of just 4, is being studied as a replacement for R134a. In the field of room air conditioners, NEDO (New Energy and Industrial Technology Development Organization) has conducted research aimed at eventual replacement of R410A with HFO-1234yf. But it was reported that the use of HFO-1234yf causes a significant decline in refrigeration system performance, and that major changes in equipment design will be required to achieve the same level of performance as current systems (Fijitaka *et al*., 2010) (Hara *et al*., 2010). Although the GWP of R32 is relatively high, at around 1/3 that of R410A, it can be used without changes to current system designs, which is a big advantage for air conditioner manufacturers. However, the current refrigeration oils for use with R410A, such as POE (Polyol ester) and PVE (Polyvinyl ether) oils, have insufficient miscibility with R32 (Ota and Araki, 2010). When the oil/refrigerant miscibility is poor, the oil tends to stay in the evaporator and not return to the compressor. This can cause a decline in system performance, and the oil return problem may lead to poor lubrication in the compressor. The authors have succeeded in developing new POE oils that eliminate this problem. In this paper we report on the characteristics of the new POE oils for use with R32.

2. PROBLEMS WITH CURRENT POE OILS

Two types of current POE oils for R410A systems (shown in Table 1) were evaluated. The phase separation temperatures of the current POE oils are shown in Figure 1. POE A (formulated using branched fatty acids) was only partially miscible with R32, and the phase separation temperature of POE B (formulated using linear fatty acids) under an R32 atmosphere was more than 30 °C higher than that under an R410A atmosphere. It was thus found that the current POE oils have poor miscibility with R32. For R32 to be used in current systems, it will be necessary to improve the miscibility of refrigeration oils with R32 to a level matching that of current oils with R410A.

As compressors have become larger and usage conditions have gotten more severe in recent years, the performance requirements for refrigeration oils have gotten tougher in terms of antiwear properties and stability. When switching from R410A to R32, an increase in the compressor discharge temperature has been reported (Taira *et al*., 2010). In developing new POE oils for the next generation of R32 systems, we must maintain the same high level of hydrolysis resistance shown by current POE oils, while improving their oil-refrigerant miscibility and antiwear properties. In addition, the demand for POE oils is rising, due to an ongoing, worldwide effort to transition from R22 systems to R410A systems. Thus, in developing new refrigeration oils for R32 systems, it is also important to use POE base oils that have good availability worldwide.

Table 1: Properties of the current POE oils

Oil			POE A (Branched)	POE B (Linear)
Kinematic Viscosity	(40℃)	mm^2/s	66.5	30.9
	(100℃)	mm^2/s	8.2	5.4
Acid Number		mgKOH/g	0.01	0.01
Pour Point		°C	-40	<-40
Additive Extreme Pressure (EP)			Use	Use
Primary use			Rotary (high pressure)	Scroll (low pressure)

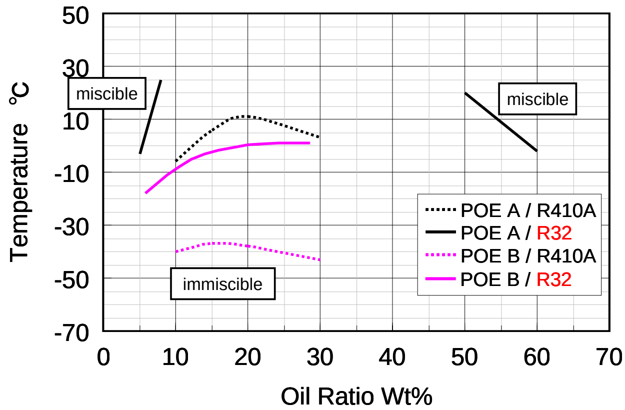


Figure 1: Phase separation temperature of current POE oils

3. DEVELOPMENT OF REFRIGERATION OILS FOR R32 SYSTEMS

3.1. Optimization of the molecular structure of POE oils

POE oils are composed by fatty acids and polyhydric alcohols such as neopentyl glycol (NPG) and pentaerythritol (PET). The performance of POE oils depends on which fatty acids and alcohols are used. We synthesized several POE oils using fatty acids with different carbon numbers and evaluated their miscibility with R32. The test results are shown in Table 2. The POE oils formulated using fatty acids with 6 or fewer carbons showed outstanding miscibility with R32. We then synthesized two types of POE oils using different branched C8 acids, each of whose molecules has a different number of branches, and evaluated their miscibility with R32. POE Type B (two branches) showed better miscibility with R32 than did POE Type A (one branch). It was found that the miscibility of POE oils was improved by increasing the number of branches in the fatty acid.

It is known that POE oils formulated with branched fatty acids show higher hydrolytic stability than POE oils formulated with linear fatty acids. Hoping to further improve the stability of POE oils, we evaluated POE oils formulated with two types of branched C9 acids in which the branches were in different positions. The stability test results for those oils are shown in Table 4. It was found that POE Type C (formulated with an alpha-branched C9 acid) showed higher hydrolytic stability than POE Type D (formulated with a beta-branched C9 acid). These results suggest that in order to create new POE oils with excellent stability and miscibility with R32, the branched fatty acid should have 1) a branch in the α-position, 2) 6 or fewer carbons, and 3) many branches. In addition, to ensure a viscosity grade of VG68 (for use in high pressure rotary and scroll compressors), it is necessary to use fatty acids with 8 or more carbon atoms. Once determining the optimum formulation, we were able to identify fatty acids that satisfy the above conditions, and develop new POE oils that offer outstanding miscibility with R32, superior stability and good availability.

Table 2: Phase separation temperature of test sample

Name	Alcohol	Fatty acids					Kinematic viscosity mm^2/s@40 °C	Phase separation temp (Oil ratio 20%, R32) °C
		C5	C6	C7	C8	C9		
		L	B	L	B	B		
H5L	PET	○					15.8	-48
H6B	PET		○				21.4	-36
H7L	PET			○			21.9	Separation
H8B	PET				○		45.3	Separation
H9B	PET					○	115.3	Separation
H8B9B (Current POE)	PET				○	○	66.5	Separation

L: Linear, B: Branched

Table 3: Phase separation temperature of test sample

Name	Alcohol	Fatty acids	Kinematic viscosity mm^2/s@40 °C	Phase separation temp (Oil ratio 20%, R32) °C
H8B Type A	PET	Branched C8 acid (one branch)	45.3	Separation
H8B Type B	PET	Branched C8 acid (two branches)	74.7	5

Table 4: Stability test results

Name	Alcohol	Fatty acids	Kinematic viscosity mm^2/s@40 °C	Acid number mgKOH/g
H9B Type C	PET	Branched C9 acid (branch in α-position)	99.7	0.01
H9B Type D	PET	Branched C9 acid (branch in β-position)	115.3	0.23
H5L	PET	Linear C5 acid	15.8	1.34
H7L	PET	Linear C7 acid	21.9	1.12

Autoclave test: 175 °C, 168 hrs, Vessel volume: 200 ml, Oil / R32 = 30 g / 30 g, Moisture in oil: 1000 ppm, Catalyst: Fe, Cu, Al.

The two newly developed POE base oils were named “RM68” and “RmM68”. The typical properties and phase separation temperatures of the new POE oils are shown in Table 5 and Figure 2. Both oils showed high miscibility with R32, equal or superior to that of current POE oils with R410A. They look promising as base oils which could be used with both the next generation R32 and the current R410A refrigerants.

Table 5: Properties of the new POE oils

Sample			RM68	RmM68	POE A
Kinematic viscosity	(40 °C)	mm^2/s	65.4	65.4	66.5
	(100 °C)	mm^2/s	7.9	8.1	8.2
Acid number		mgKOH/g	0.01	0.01	0.01
Phase separation temp. (R32)		℃	-15	9	Separation
Phase separation temp. (R410A)		℃	<-50	-31	11
Availability			Good	Good	Excellent

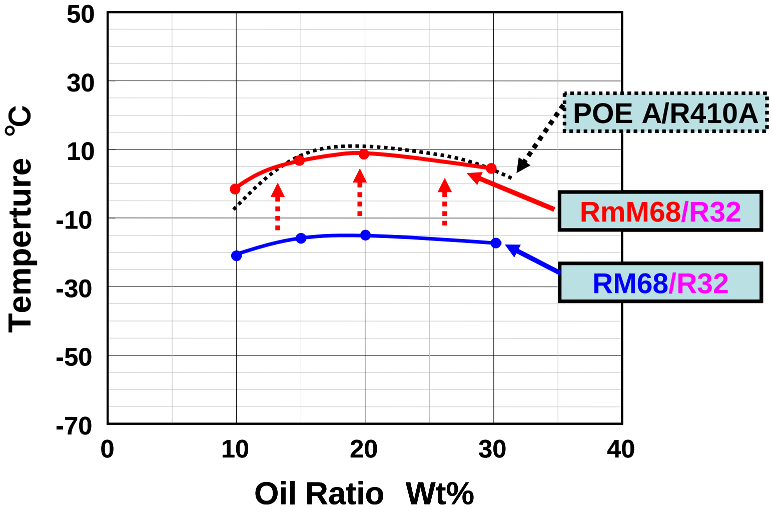
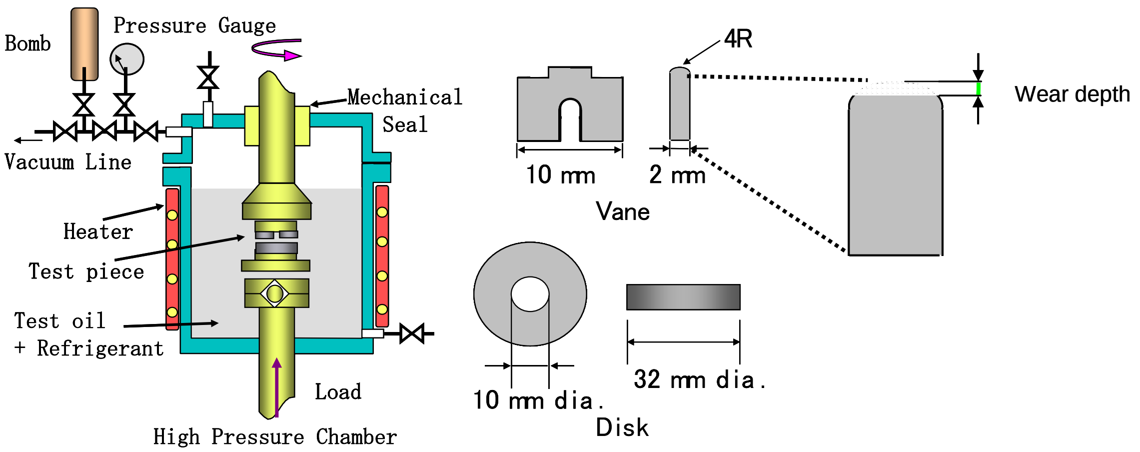


Figure 2: Phase separation temperature of new POE oils

3.2 Improving the antiwear properties of POE oils

Lubricity tests were performed using a high-pressure tribometer and test pieces (shown in Figure 3). When the test was complete, vane wear depth was measured and the antiwear properties of the test oils were evaluated. Using EP additives is normally effective for improving antiwear properties, but with POE oils it is known that EP additives in the oil do not adsorb well on the sliding surfaces of parts. The performance-improving effect is therefore small. Even with POE oils, it is possible to achieve better antiwear properties by increasing the amount of EP additives. However, increasing the amount of EP additives may lead to a decline in stability, meaning it is not easy to achieve both good lubricity and stability simultaneously. A known method for improving the effects of phosphorus EP additives in POE oils is to use EP additives in combination with an assistant (agent) that is easily adsorbed on metal surfaces, such as benzotriazole. With this method, the amount of phosphorus EP additives adsorbed on the sliding surfaces is increased. Hoping to further improve antiwear performance, we set out to identify new assistants that would improve the adsorption capacity of phosphorus EP additives even more than benzotriazole. Table 6 shows the results of wear tests using various combinations of EP additives and assistants. Using new assistant A, the adsorption capacity of the phosphorus EP additive was improved. Testing showed that this combination gave the highest antiwear performance.

“RM68EA” and “RmM68EA” were developed using the new POE oil and new additive combination. The wear test results for RM68EA and RmM68EA are shown in Figure 4. Both RM68EA and RmM68EA showed much better antiwear performance than a current POE A (with EP additive). The results of vane surface analysis are shown in Figure 5. It was found that RM68EA formed a stronger tribofilm on the sliding surface than POE A, and exhibited excellent antiwear properties.



Test temperature: 110 °C, Test time: 60 min, Test piece: Vane (SKH51), Disk (FC250)

Figure 3: Tribometer and test piece

Table 6: Wear test results for test samples (under R32 atmosphere)

Sample	Base oil	EP additive	Assistant additive	Vane wear depth, μm
1	RM68	None	None	13.5
2	RM68	TCP	None	8.5
3	RM68	None	Benzotriazole	10.3
4	RM68	TCP	Benzotriazole	6.8
5	RM68	TCP	Benzotriazole derivative	7.5
6	RM68	TCP	New assistant A	4.0
7	RM68	TCP	New assistant B	6.5
8	RM68	TCP	New assistant C	5.9

TCP: Tricresyl phosphate

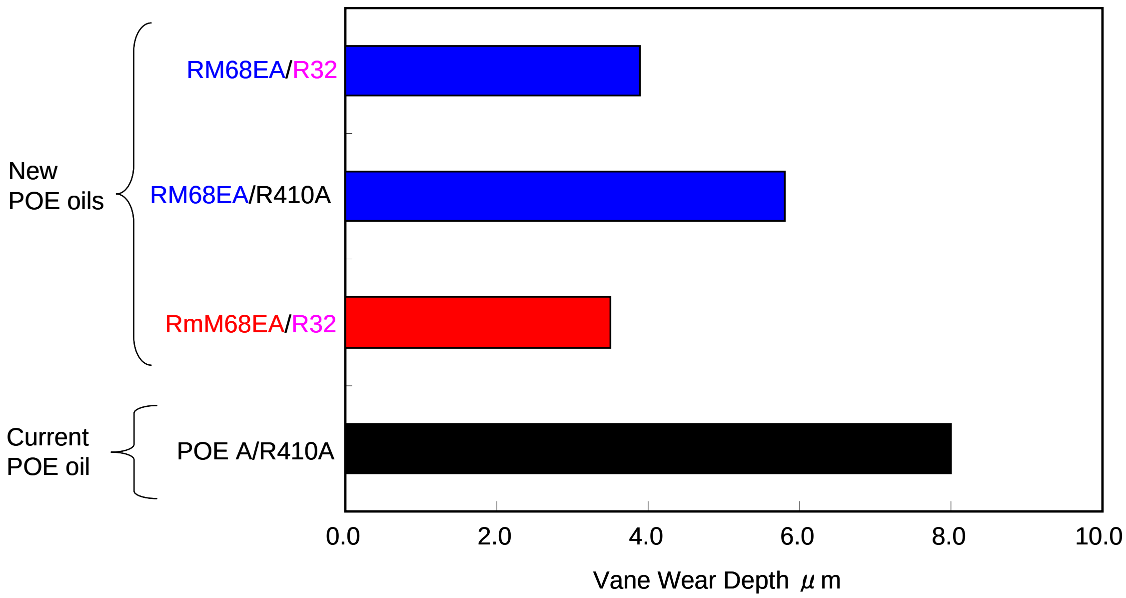
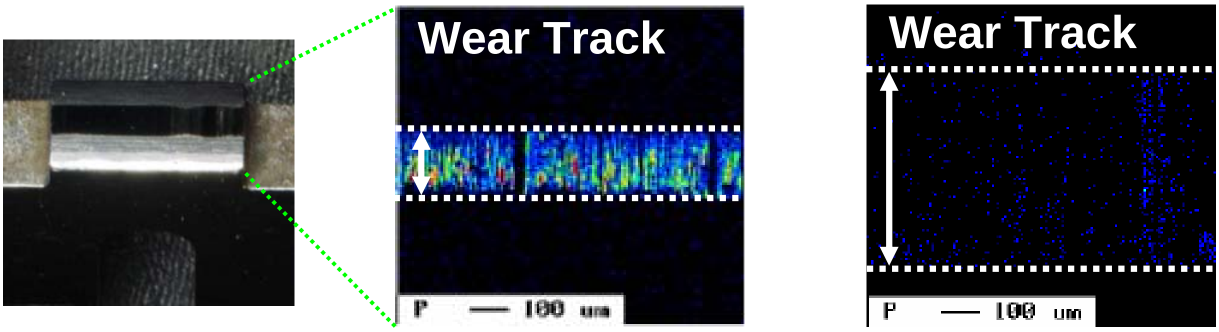


Figure 4: Wear test results for new POE oils

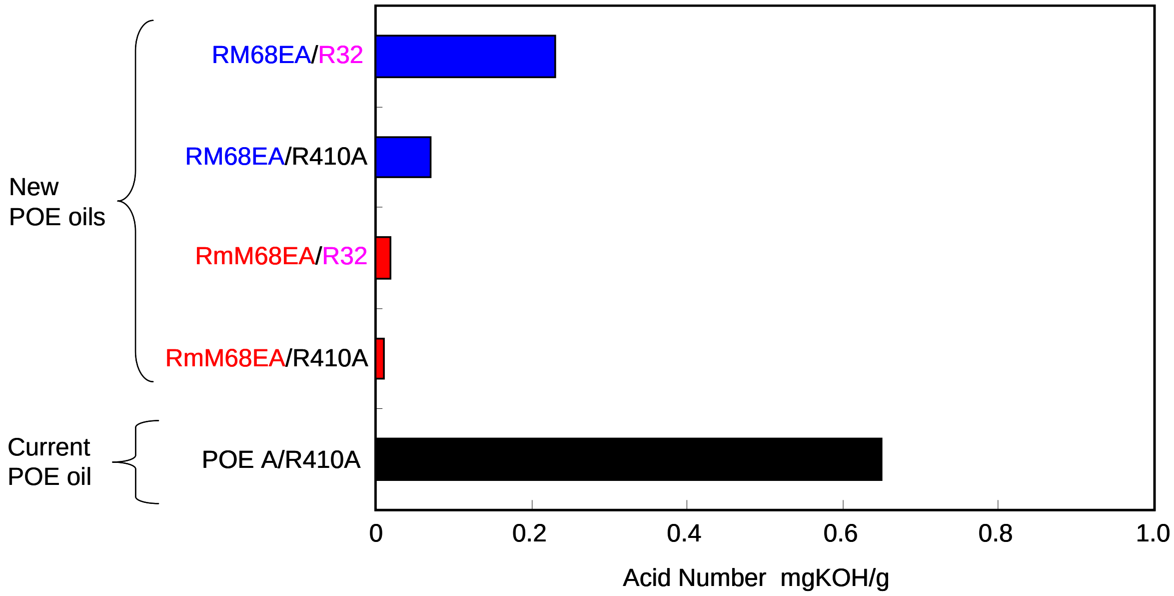


RM68EA (new additive combination)   POE A (with EP additive)

Figure 5: EPMA analysis result of vane test piece

3.3 Stability of POE oils

The stability test involved testing at 175 °C for 168 hours. The stabilities of the new POE oils were evaluated and compared with that of a current POE oil for R410A systems. The stability test results for RM68EA and RmM68EA are shown in Figure 6. RM68EA and RmM68EA showed greater stability than POE A under both R32 and R410A atmospheres. The new POE oils were found to be excellent refrigeration oils that could be used with both the next generation R32 and current R410A refrigerants.



Autoclave test: 175 °C, 168 hrs, Vessel volume: 200 ml, Oil / Refrigerant = 30 g / 30 g, Moisture in oil: 1000 ppm , Catalyst: Fe, Cu, Al.

Figure 6: Stability test results for new POE oils

4. PROPERTIES OF NEW POE OILS

The typical properties of the new POE oils are shown in Table 7. Oils have been developed in viscosity grades from VG32 to VG68. Higher viscosity oils are being developed for use in a wider range of compressors, including low pressure scroll, high pressure scroll, and high pressure rotary models. The new POE oils have been tested by compressor manufacturers around the world and shown to provide superior antiwear performance.

Table 7: Properties of new POE oils

			New POE oils					Current POE oils	
Name			RM32	RM46	RM56	RM68	RmM68	POE B	POE A
Viscosity grade			VG32	VG46	VG56	VG68		VG32	VG68
Kinematic viscosity	(40℃)	mm^2/s	32.7	45.7	55.0	65.4	65.4	30.9	66.5
	(100℃)	mm^2/s	5.2	6.3	7.1	7.9	8.1	5.4	8.2
Acid number		mgKOH/g	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Phase separation temp. (R32)		°C	-42	-48	-34	-15	9	1	Separation
Phase separation temp. (R410A)		°C	<-50	<-50	<-50	<-50	-31	-37	11
Target			Scroll (low pressure) Reciprocating			Rotary (high pressure) Scroll (high pressure)		Scroll (low pressure) Reciprocating	Rotary (high pressure) Scroll (high pressure)

VG: Viscosity grade

5. CONCLUSION

A problem with current refrigeration oils for R410A systems is that they have poor miscibility with R32, which is a leading candidate to be the refrigerant for the next generation of air conditioners. Hoping to solve this problem, we tested POE oils with modified molecular structures and were able to develop new POE oils that showed outstanding miscibility with R32. Another problem is the inferior lubricity of POE oils. When used in POE oils, EP additives do not adsorb well on sliding surfaces and thus antiwear performance is lacking. To overcome this problem, we developed a new assistant (additive) that promotes the adsorption of EP additives, and found that it greatly improved the antiwear performance of POE oils. The new POE oils were developed by combining these technologies. These new refrigeration oils can be used with both next generation R32 and current R410A refrigerants.

6. REFERENCES

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