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Hitoshi Takahashi
JX Nippon Oil & Energy Corporation, Japan, hitoshi.takahashi@noe.jx-group.co.jp

Katsuya Takigawa
JX Nippon Oil & Energy Corporation, Japan, katsuya.takigawa@noe.jx-group.co.jp

Takeshi Okido
JX Nippon Oil & Energy Corporation, Japan, takeshi.okido@noe.jx-group.co.jp

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Takeshi Okido*, Katsuya Takigawa, Hitoshi Takahashi

JX Nippon Oil & Energy Corporation
8, Chidoricho, Naka-ku, Yokohama, 231-0815, Japan
E-mail: takeshi.okido@noe.jx-group.co.jp

* Corresponding Author

ABSTRACT

R32 has been applied as an air-conditioner refrigerant in Japan for a few years. Although its GWP is slightly higher than the limit of F-gas restriction, high COP is a key driving force for R32 system.
Regarding refrigeration oil applied to R32, there are two main issues. First issue is miscibility with R32, because incumbent refrigeration oil for R410A is rather immiscible to R32. Second issue is lubricity. When refrigerant is miscible well with refrigeration oil, generally, dissolved refrigerant reduce viscosity of refrigerant-oil mixture. Lower viscosity results in lower lubricity, and finally, it would cause wear of sliding parts, compressor durability shortage, insufficient sealing, or reduced COP.
At the earlier stage, several refrigeration oils miscible with R32 have been proposed. However, we have experienced wearing problems on surface of a main shaft in R32 system with such refrigeration oils, for example. Those problems were not found in R410A systems. We assumed there is some different mechanism on sliding parts in R32 systems comparing with current refrigerant systems.
We focused on viscosity of refrigerant - oil mixture, which could be correlated to lubricity. Then, we found that viscosity of R32 - refrigeration oil mixture is extremely lower than that of R410A - refrigeration oil. Together with results of wearing problem in sliding parts, which are not worn by fluid lubrication in general, we assumed that oil film is formed insufficiently on the surface due to the extreme low viscosity of the mixture.
Our goal of development of refrigeration oil for R32 was reset to balance miscibility and lubricity, which is trade-off normally. Through various studies, finally, we found a new base oil to meet our goal, which makes us possible to achieve not only high viscosity of the mixture, but also good miscibility with R32. Its excellent characteristics on lubricity and miscibility are also confirmed by several compressor tests.

1. INTRODUCTION

In recent years the effect on global warming of refrigerant used in the refrigeration equipment is focused when it has leaked into the atmosphere. Since R410A, refrigerant used in air conditioners, has high GWP (Global Warming Potential) of roughly 2000 (About 2000 times that of carbon dioxide), various alternative refrigerants have been studied. Although the GWP of R32 is relatively high, around 600, it draws attention as a substitute of R410A due to improvement of system performance and ease of handling as a single refrigerant. The first air conditioner applied to R32 was released in Japan in 2012.
From a viewpoint of refrigeration oil, it has been reported that the polyol ester (POE) oil and polyvinyl ether (PVE) oil, which are widely used as refrigeration oil for the present R410A, 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 to return to the compressor. This can cause a decline in system performance or poor lubrication in the compressor. To solve this problem, various development works was done. As a result, new POE and PVE oils which have superior miscibility with R32 were developed (Okido et al., 2012) (Matsumoto et al., 2012). These new oils became an aid of launch of the first air conditioner applied to R32. On the other hand, as a result of investigating the various performances of new POE oil under R32 atmosphere, the new issue which was not seen at the time of R410A systems was found. The solution to this issue was studied and the result was reported in this paper.

2. TEST METHOD

The miscibility of test sample was evaluated by the test method defined in JIS K2211. The stability of test sample was evaluated by the autoclave test defined in JIS K2211. The measurements of both refrigerant ratio in oil and kinematic viscosity of oil with refrigerant were carried out using a measuring device shown in Fig.1. Refrigerant and oil were put into the pressure vessel, and heated to the target temperature. Then, the measurement was performed after adjusting the amount of refrigerant to the target pressure. The refrigerant ratio in oil was calculated from the amount of oil and refrigerant in vessel. The kinematic viscosity of oil with refrigerant was measured by the viscosity sensor attached to the vessel.

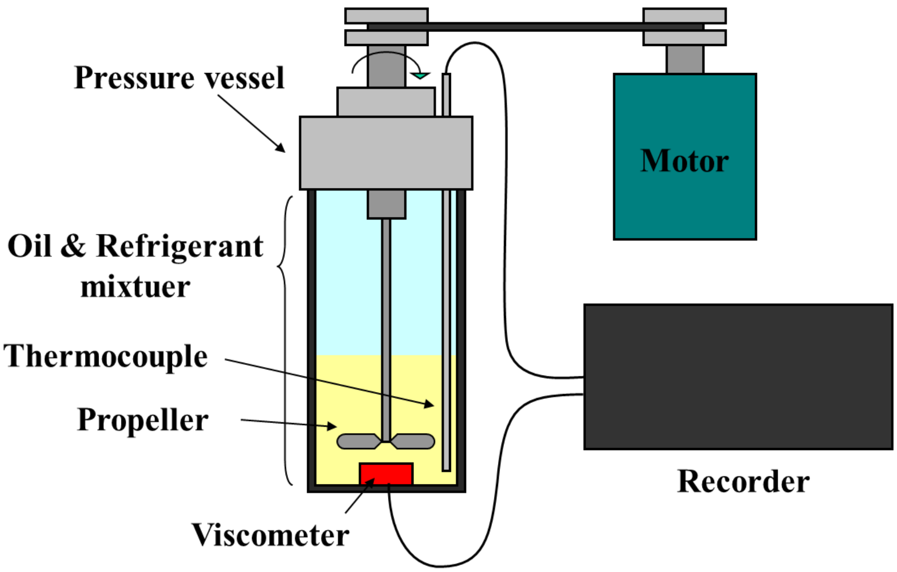

Figure 1: Kinematic viscosity (with refrigerant) measuring device

3. ISSUES WITH R32 SYSTEMS

Miscibility, stability, and lubricity are typical properties when refrigeration oil is evaluated. The properties of new refrigeration oil "POE-1", which have better miscibility with R32 than the present oil for R410A "POE A", are shown in Table 1.

Table 1: Properties of the new POE oil

Sample			POE-1	POE A
Viscosity Grade			VG68	VG68
Kinematic Viscosity	(40℃)	mm^2/s	65.4	66.5
	(100℃)	mm^2/s	7.9	8.2
Phase Separation Temp.(R32)		℃	-15	Separation
Phase Separation Temp.(R410A)		℃	<-50	11

The stability of POE-1 under R32 atmosphere was evaluated. The stability test results for POE-1 and POE A are shown in Table 2. POE-1 showed the same stability compare with present oil POE A for R410A.

Table 2: Stability test result for new POE oil

Sample	POE-1	POE A
Refrigerant	R32	R410A
Acid Number (After Stability Test) mgKOH/g	0.01	0.01

Autoclave test：175 ℃, 168 hr, Vessel volume: 200ml, Oil / Ref = 30g / 30g, Moisture in oil：1000ppm , Catalyst: Fe, Cu, Al.

In lubricity, the sliding part in a compressor is generally classified into fluid lubrication (shaft / bearing) and mixed lubrication (vane / roller). When R32 was applied, it was found that wear in the sliding part in this fluid lubrication occurs more often compared with the time of R410A use. In the fluid lubrication, the sliding parts don't contact one another through an oil film, and the oil film becomes thicker as the kinematic viscosity of the intervening oil becomes higher. The main cause of wear in the R32 system is possibly assumed that the sufficient oil film thickness was not secured due to smaller kinematic viscosity of the oil / R32 mixture. We measured the kinematic viscosity of POE-1 / R32 and POE A / R410A under the same temperature and pressure conditions. The results are shown in Table 3.

Table 3: Kinematic viscosity of new POE oil with refrigerant

Sample	POE-1 / R32	POE A / R410A
Kinematic Viscosity mm^2/s	5.0	5.3
Refrigerant ratio in oil %	16.0	18.5

Temperture：60 ℃, Pressure: 2.1MPa,

Although POE-1 / R32 had less amounts of refrigerant dissolution compared with POE A / R 410A, it was found that kinematic viscosity of POE-1 / R32 became lower than that of POE A / R410A. From these results, it was presumed that R32 has the characteristic to decrease the kinematic viscosity of oil when mixed with refrigeration oil, compared with R410A. Then, we measured the kinematic viscosity at 60C when equal amount of R32 and R410A were dissolved in POE A. The results are shown in Table 4.

Table 4: Kinematic viscosity of POE A with refrigerant

Sample	POE A	POE A / R32 (Refrigerant ratio in oil 10%)	POE A / R410A (Refrigerant ratio in oil 10%)
Kinematic Viscosity (60℃) mm^2/s	27.3	8.9	9.7

The kinematic viscosity of POE A with 10% of R410A dissolved fell from 27.3 mm^2/s to 9.7 mm^2/s, whereas the kinematic viscosity of oil with 10% R32 dissolved fell to 8.9 mm^2/s. From these results, the presumption turned out to be correct that R32 is easy to reduce kinematic viscosity when dissolved in refrigeration oil compared with present refrigerant R410A. To eliminate the possible cause of wear in the mixture of smaller kinematic viscosity, we started to develop POE of less kinematic viscosity decrease at the time of R32 dissolution.

4. DEVELOPMENT OF IMPROVED REFRIGERATION OILS FOR R32 SYSTEMS

4.1 Improvement of the kinematic viscosity of POE oils with R32

We focused on the ester compounds containing POE oils, which had sufficient record in market as refrigeration oil for HFC and showed stable supply worldwide. Ester compounds are composed of fatty acids and alcohols.

The performance of ester compounds depends on selection of fatty acids and alcohols. The development goal was determined that a new ester compound is more miscible and has higher kinematic viscosity under R32 atmosphere than POE A / R410A combination. POE A has been applied for R410A for more than decade without any problem. As mentioned, when oil / refrigerant miscibility is poorer, the oil tends to stay in the evaporator and not to return to the compressor. This can cause decline in system performance or poor lubrication in the compressor. In the case the kinematic viscosity of oil / refrigerant mixtures is lower, sufficient oil film cannot be formed at the sliding portion, and the wear is likely to occur. For the reason noted above, the development goal was determined. We synthesized several POE oils with modified molecular structures, and measured their phase separation temperature and kinematic viscosity under R32 atmosphere. The results are shown in Table 5 and Fig. 2. Although there was a sample close to development target, we could not achieve it because of trade-off relationship between miscibility with R32 and kinematic viscosity of the oil / R32 mixture.

Table 5: Phase separation temp. & kinematic viscosity (with refrigerant) of new POE oils

Sample		POE-1	POE -2	POE-3	POE-4	POE-5	POE-6	POE A
Viscosity Grade		VG68	VG68	VG68	VG75	VG46	VG56	VG68
Phase Separation Temp. (R32)	℃	-15	9	19	16	-48	-34	Separation
Kinematic Viscosity (R32 2.1MPa 60℃)	mm^2/s	5.0	5.2	6.0	6.2	4.0	4.3	6.4

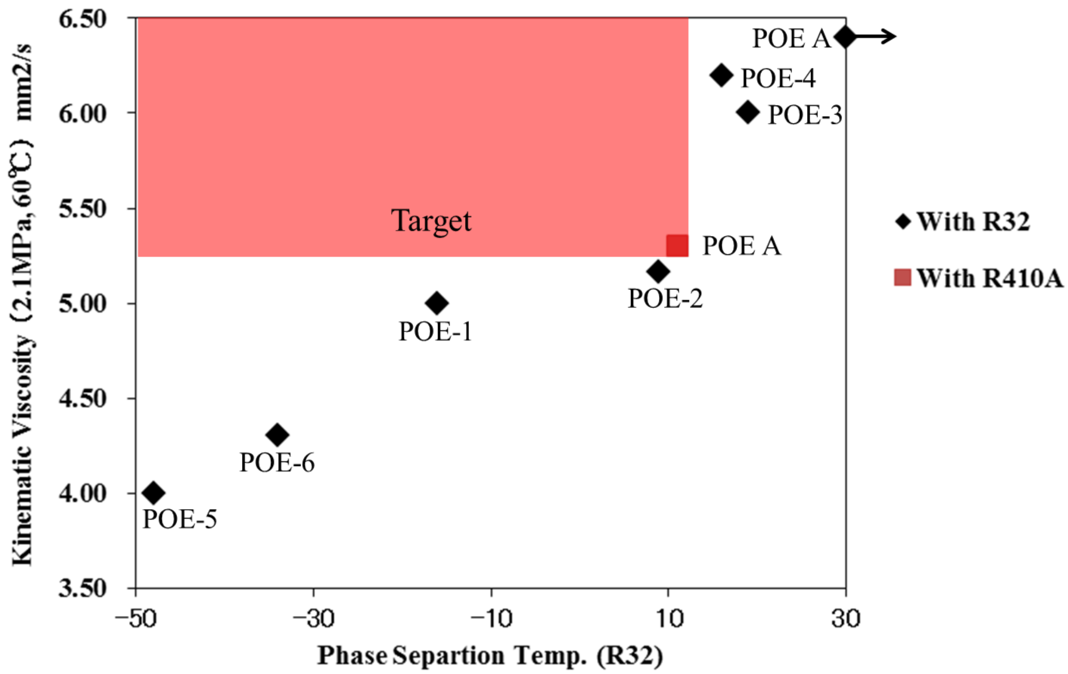

Figure 2: Phase Separation Temp. & Kinematic Viscosity (with refrigerant) of new POE oils

4.2 Application of new ester compound

It was difficult to achieve the development goal using POE oils with modified molecular structures, therefore we decided to investigate ester compounds other than POE. POE is a reactant of multivalent polyhydric alcohols and monovalent organic acids. As ester compounds other than POE, there are the reactants of the multivalent organic acids and various alcohols. As a result of synthesizing various ester compounds, we developed new esters with high kinematic viscosity at high temperature range in spite of the same viscosity grade at 40C. Phase separation temperature and kinematic viscosity of new esters under R32 atmosphere were measured. The results are shown in Table 6.

Table 6: Phase separation temp. & kinematic viscosity (with refrigerant) of New esters

Sample			New ester 1	New ester 2	New ester 3	POE A
Viscosity Grade			VG68	VG68	VG68	VG68
Kinematic Viscosity	(40℃)	mm^2/s	67.6	67.6	67.8	66.5
	(100℃)	mm^2/s	10.3	10.6	10.6	8.2
Phase Separation Temp.(R32)		℃	Separation	Separation	Separation	Separation
Kinematic Viscosity (R32 2.1MPa 60℃)		mm^2/s	8.0	7.8	7.5	6.4

Although New esters showed poor miscibility with R32, the kinematic viscosity with R32 dissolution was markedly higher than that of POE A. Then, New ester 3, which showed the best miscibility with R32 among new esters, was blended with POE-1, which had superior miscibility with R32 to make "new Developed oil". We measured the phase separation temperature and kinematic viscosity of the new Developed oil under R32 atmosphere. The results are shown in Table 7 and Fig. 3. It was found that the new Developed oil blended with new ester 3 showed remarkably higher kinematic viscosity under R32 atmosphere than conventional POE. The effect of the improvement in kinematic viscosity with refrigerant was confirmed also by several compressor tests conducted by our customers and lubricity in the fluid lubrication area such as between shaft and bearing was improved dramatically.

Table 7: Phase separation temp. & kinematic viscosity (with refrigerant) of the new Developed oil

Sample			New Developed oil (POE-1＋new ester 3)	POE-1
Viscosity Grade			VG68	VG68
Kinematic Viscosity	(40℃)	mm^2/s	63.8	65.4
	(100℃)	mm^2/s	8.9	7.9
Phase Separation Temp.(R32)		℃	6	-15
Kinematic Viscosity (R32 2.1MPa 60℃)		mm^2/s	6.3	5.0

The stability of the new Developed oil under R32 atmosphere was evaluated. The result is shown in Table 8. The new Developed oil showed the same stability compare with present oil POE A for R410A.

Table 8: Stability test result for new Developed oil

Sample	New Developed oil	POE A
Refrigerant	R32	R410A
Acid Number (After Stability Test) mgKOH/g	0.01	0.01

Autoclave test：175 ℃, 168 hr, Vessel volume: 200ml, Oil / Ref = 30g / 30g, Moisture in oil：1000ppm, Catalyst: Fe, Cu, Al.

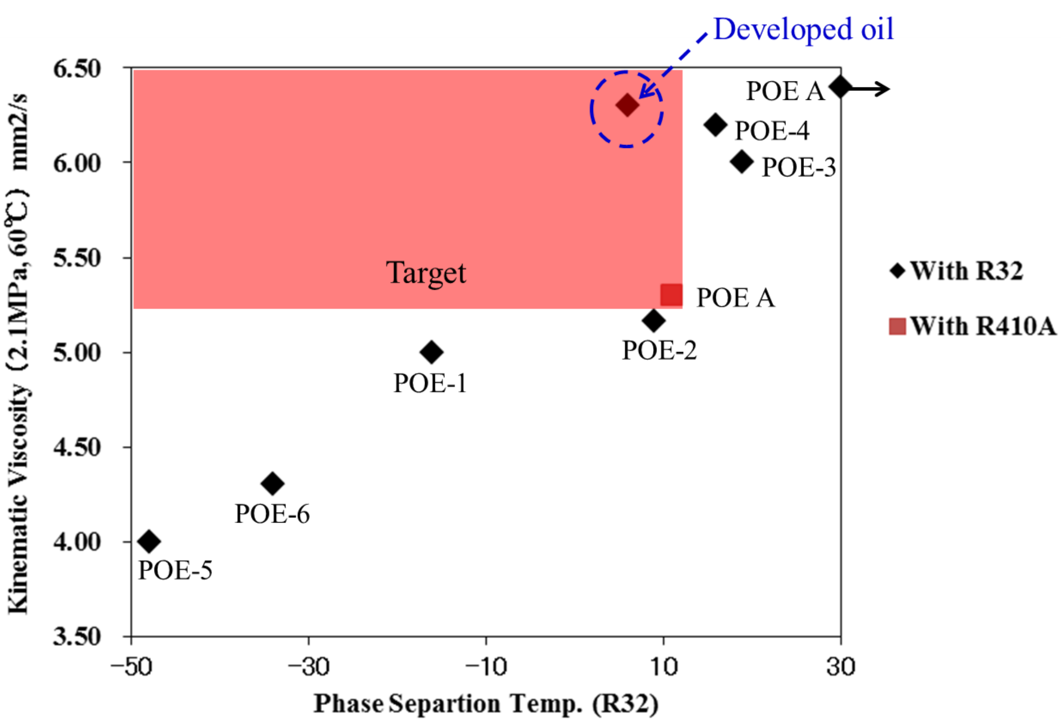

Figure 3: Phase separation temp. & kinematic viscosity (with refrigerant) of the new Developed oil

5. CONCLUSION

Since R32 has less greenhouse effect and improves system performance compared with R410A, it is a leading candidate refrigerant for next generation air conditioners. However, it was found that when R32 was dissolved in refrigeration oils, the kinematic viscosity of refrigeration oils were reduced remarkably compared with when present R410A was dissolved. To solve this issue of trade-off between miscibility and lubricity, we synthesized various ester compounds and evaluated the performance. As a result, a new ester was developed, which showed much higher kinematic viscosity with R32 dissolved compared with conventional POE. From now on, further development of the refrigeration oil for R32 which has excellent miscibility, lubricity, and stability will be expected by utilizing this new ester.

6. REFERENCES

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