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POE Lubricant Candidates For Low GWP Refrigerants

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ABSTRACT

Several series of polyol ester (POE) refrigeration lubricants have been investigated for low GWP refrigerant R32 (R-410A replacement) and HFO-1234ze (R-134a replacement). The main problems of R32/HFO refrigeration lubricant development can be summarized as balancing between miscibility, solubility and lubricity. Generally speaking, refrigerant-lubricant mixture with highly miscible property in low temperature evaporator will lead to more soluble phenomenon in high temperature compressor. Therefore, when refrigerant is well miscible with refrigeration lubricant, dissolved refrigerant will reduce working viscosity of refrigerant-oil mixture in compressor, and thus results in lower lubricity, wear of sliding parts, and compressor durability shortage. In our studies, the key factor which result in aforementioned phenomenon was found, and can be controlled independently by using optimized chemical structure.

For R32 compressor system, we have successfully developed a series of POE refrigeration lubricant, with viscosities ranging from 32cSt to 90cSt at 40°C, and with a wide range of miscibility (20% oil) from -40℃ to 2℃. From results of PVT experiments and lubricity tests (Falex P/V and four ball), it demonstrated to be possible to develop a POE oil with high miscibility, low solubility and high working viscosity. All results in R32 system were better than traditional refrigeration lubricant in R410A system. Meanwhile, we also were able to identify the relationship between surface tension of chemical structure and lubricity.

For HFO-1234ze compressor system, incumbent refrigeration lubricants suitable for R134a are almost fully miscible in HFO-1234ze, which could lead to severe refrigerant dilution of lubricant viscosity and poor lubricity due to high solubility. Through studies of chemical structure of refrigeration lubricants, reliable experimental tests and rigorous thermodynamic calculation, we created a range of POE lubricants (ISO68 to ISO220) with miscibility (20% oil) from -33℃ to -13℃, all the while, maintaining solubility and working viscosity on par with the common POE refrigeration lubricants currently used in R-134a system.

1. INTRODUCTION

Global warming issues and related regulations, such as EU's F-gas regulation, promote the conversion of commercial refrigerant to next generation refrigerant with low GWP; consequently, it creates a need for designing a new structure of refrigeration lubricant to work with low GWP refrigerants. In this paper, we will investigate polyol ester (POE) refrigeration lubricants for R32 (R-410A replacement) and R1234ze (R134a replacement).

R32 is one of the HFC refrigerant with relative low GWP, but its main problem is immiscible in the existence refrigeration lubricant for R410A. To solve this problem, several papers have been published (Tomita *et al*., 2015) (Matsumoto *et al*., 2015). However, the miscibility isn't the only one problem of R32. In the R32 working applications, the high discharge temperature and pressure cause gear and bearing subjected to high loads. It is important that the lubricants being used possess the ability to protect against abnormal gear and bearing wear in boundary condition. To protect the compressor in R32 system, developing the refrigeration lubricant for R32 not only good miscibility but also high lubricity must be considered.

R1234ze is the other low GWP refrigerant solution. Opposite to R32, it's almost full range miscible in commercial refrigeration lubricant for R134a. Generally speaking, good miscible ability may lead to high refrigerant solubility, and causes too much refrigerant dissolving into lubricant under compressor operation. The dissolved refrigerant may substantially lower the viscosity of the oil-rich phase, resulting in lower lubrication properties and giving rise to a potential breakdown of the compressor mechanical parts. The other problem of high solubility is that it will reduce the efficiency of oil separator in refrigeration system.

Development refrigeration lubricants can be summarized as balancing miscibility, solubility and lubricity. In our studies, the key factors which result in aforementioned phenomenon were found, and can be controlled independently by using optimized chemical structure.

2. EXPERIMENTAL

2.1 Lubricant Synthesis

We choose the POE lubricants as our low GWP refrigerants solution. Esterifying the polyol with the different linear or branched acid afforded refrigeration lubricants. Utilizing Gibbs free energy calculation, we can optimize the chemical structures by correlating miscibility, solubility and working viscosity data. The surface tension can be estimated by parachor parameter (Hansen, 2007, Goel, 2006). According to these parameters, we can design the best structure for target refrigerants.

2.2 Lubricity

In compressor applications, gear and bearing are subjected to high loads. The extreme pressure properties of POE is important when high-load conditions are encountered. We measure the EP properties of POE by using Falex Pin & Vee block test machine under ASTM D3233 method and modified temperature of 80℃.

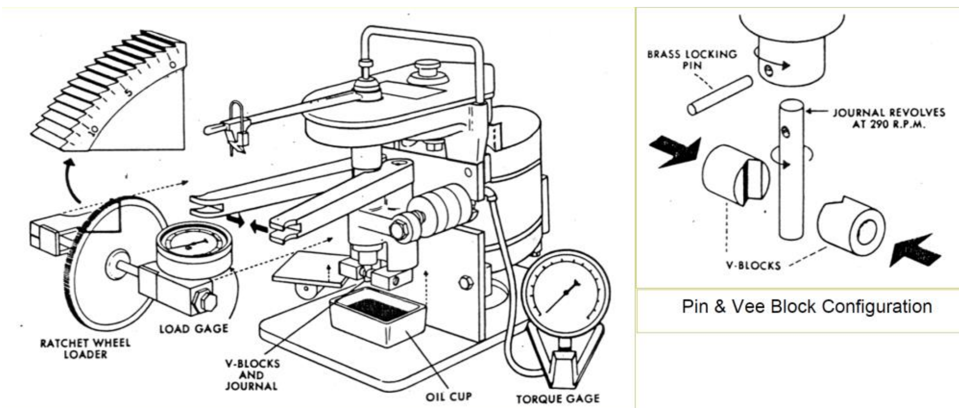

Figure 1: Falex Pin & Vee Block test machine, picture from Falex

2.3 Miscibility

Following the ASHRAE 86-1994 method by using in-house seal instrument, miscibility test can be conducted with oil percent ranging from 5~30 wt% of mixture. Alternating the environment temperature of seal tube to observe the oil-refrigerant mixture phenomenon till separating into two phases in the tube, and then recording miscibility temperature.

2.4 Solubility and Working Viscosity

An experimental test facility has been constructed, tested and calibrated for measurement of lubricant refrigerant mixture properties. The lubricant is first charged into the test system (±0.1 grams) and then the refrigerant is charged (±0.1 grams) into test system under condition: -10℃ and high vacuum. The mixture system is stirred and heated to suitable temperature based on the type of refrigerant. Sampling and measuring the related solubility, viscosity and density data only when vapor-liquid equilibrium has been achieved in mixture system. The numbers of measuring for each specified refrigerant-lubricant mixture are around 45~50 points.

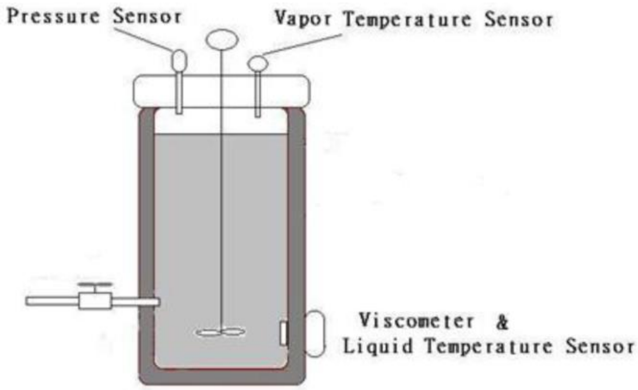

Figure 2: Viscosity and solubility test system

3. REFRIGERANTION LUBRICANTS FOR R32

3.1 The Lubricity and Surface Tension

The studies have demonstrated that the frictional properties of oil-films are directly influenced by cohesive energy. (Lee *et al*., 2000) The cohesive forces among liquid molecules are related to the phenomenon of surface tension. We can calculate the surface tension by the parachor parameter from chemical structure (Goel, 2006). The equation of surface tension listed in equation (1).

$$\gamma = (P/Vm)^4 \tag{1}$$

γ is surface tension, P is parachor parameter, Vm is molar volume

In Table 1 and Figure 3, we find some relationship between extreme pressure properties and surface tension. It can predict the lubricity tendency of refrigeration lubricant when we design a new chemical structure.

Table 1: The extreme pressure properties and surface tension

Typical value		Traditional fully branched POE	R32-A	R32-B	R32-C	R32-D	Traditional Mixed acid POE	R32-E
Test item	unit							
Viscosity Grades		ISO-68					ISO-32	
Kinetic Viscosity @40℃	cSt	68	68	68	68	68	32	32
Viscosity index		90	102	122	122	118	120	130
Surface tension @80℃	Dyne/cm	26.60	28.22	29.31	29.43	29.50	28.28	29.37
Falex P/V load to failure modified 80℃	lbs	748	1058	1326	1170	1267	1002	1380

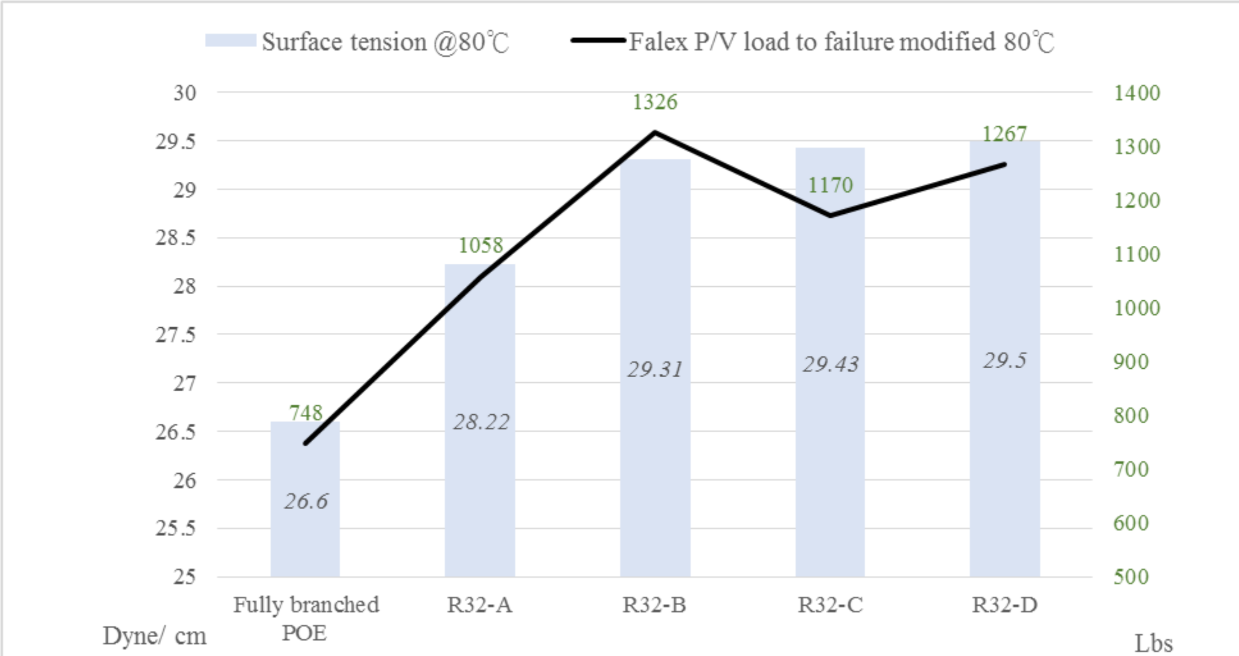

Figure 3: Variation of surface tension & extreme pressure properties for ISO-68 oils

3.2 Miscibility of R32 Refrigeration Lubricants

Based on investigation above, we design a series of refrigeration lubricants for R32 with good lubricity. Following ASHRAE 86-1994 method, we conduct the synthetic refrigeration lubricant's miscibility tests. Controlling the ratio of fatty acid, we can alter chemical structure to adjust the miscibility in the same viscosity grade. Test results are shown in Table 2 and Figure 4.

Table 2: The miscibility of R32 refrigeration lubricants

Typical value		Traditional fully branched POE	Traditional mixed acid POE	R32-A	R32-B	R32-C	R32-D	R32-E	R32-F
Test item	unit								
Kinetic Viscosity @40℃	cSt	68	68	68	68	68	68	32	93
Miscibility, 20% oil in R32	℃	immiscible	immiscible	2	2	-20	-40	-22	-19

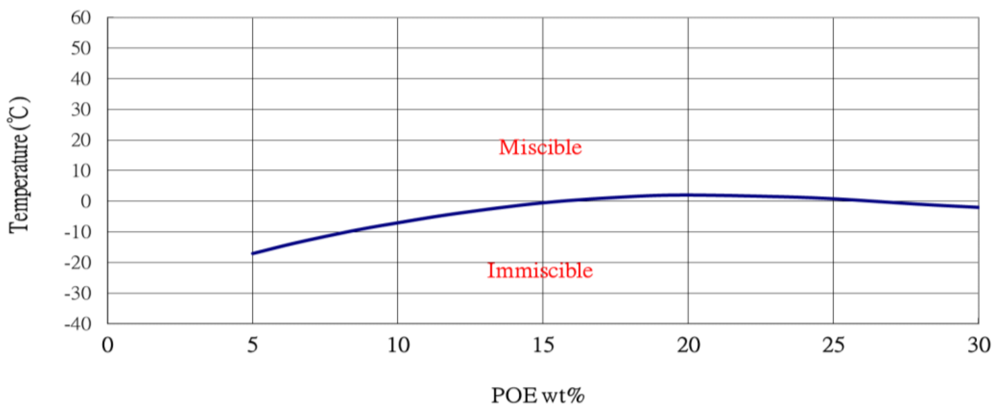

Figure 4: Miscibility chart of R32-A in R32 (ISO-68)

3.3 Solubility and Working Viscosity of R32 Refrigeration Lubricants

The synthetic oils are measured by the instrument we constructed, recording the viscosity, temperature, density and pressure value, and utilizing the simulation model (Hung et al., 2015) to draw the P-V-T diagram. Based on ASHRAE standard working condition (Condenser temp. 54.4℃, Discharge Temp. 115℃, Bearing Temp. 90-95℃, Sump Pressure 3473kPa, Calculating Temp. 95℃), calculating the working viscosity in the R32 system and shown in Table 3. In Figure 5, it shows that the miscibility is not proportional related to solubility.

Table 3: Working viscosity of R32 refrigeration lubricants (ISO-68)

Typical value		R32-B	R32-C	R32-D
Test item	unit			
Kinetic Viscosity @40℃	cSt	68	68	68
Miscibility, 20% oil in R32	℃	2	-20	-40
Solubility	Wt%	14.05	13.3	14.74
Working viscosity	cSt	2.82	2.91	2.73

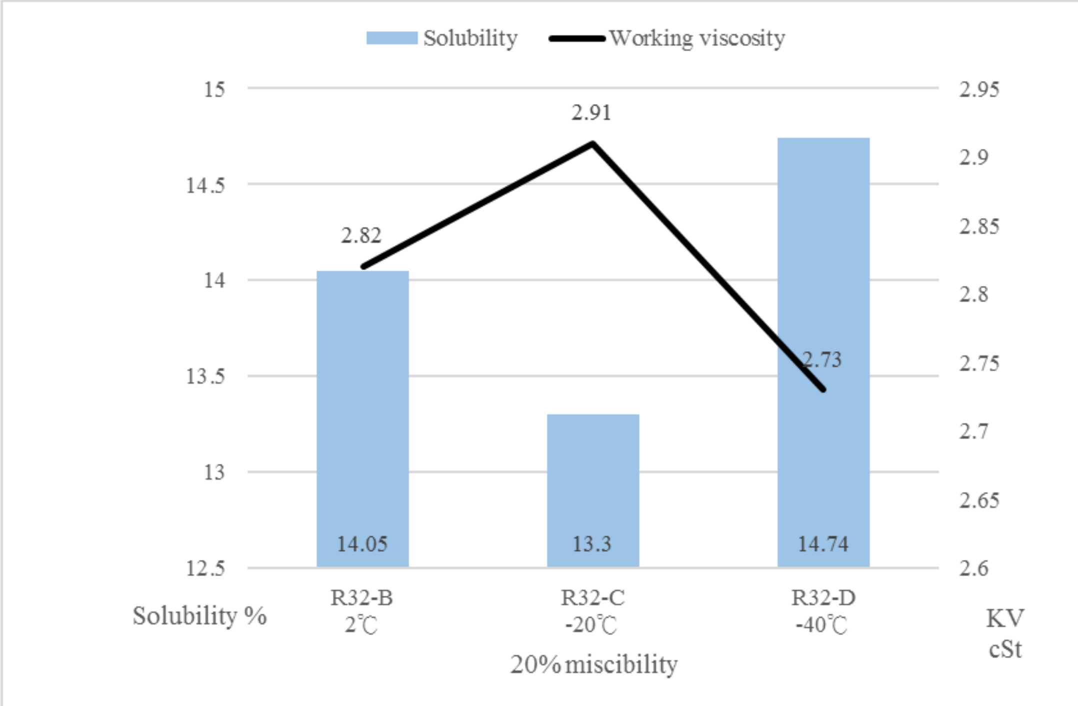

Figure 5: Miscibility, solubility and working viscosity of R32 refrigeration lubricants (ISO-68)

4. REFRIGERANTION LUBRICANTS FOR R1234ZE

4.1 The Miscibility of R1234ze Refrigeration Lubricants

Opposite to R32, R1234ze compressor working condition is in the relative low pressure. The high dilution of refrigeration lubricant has much impact on extreme pressure properties. We select different raw materials to synthesize a series of POE with wide viscosity range and control the miscibility over -40℃. Test results are shown in Table 4 and Figure 6.

Table 4: The miscibility of R1234ze refrigeration lubricants

Typical value		Traditional fully branched POE	Traditional mixed acid POE	R1234ze-A	R1234ze-B	Traditional fully branched POE	R1234ze-C	R1234ze-D	R1234ze-E
Test item	unit								
Kinetic Viscosity @40℃	cSt	68	68	68	68	220	220	170	100
Viscosity index		90	120	124	159	90	123	131	149
Miscibility, 20% oil in R1234ze	℃	<-60	<-60	-13	-32	<-60	-14	-33	-33

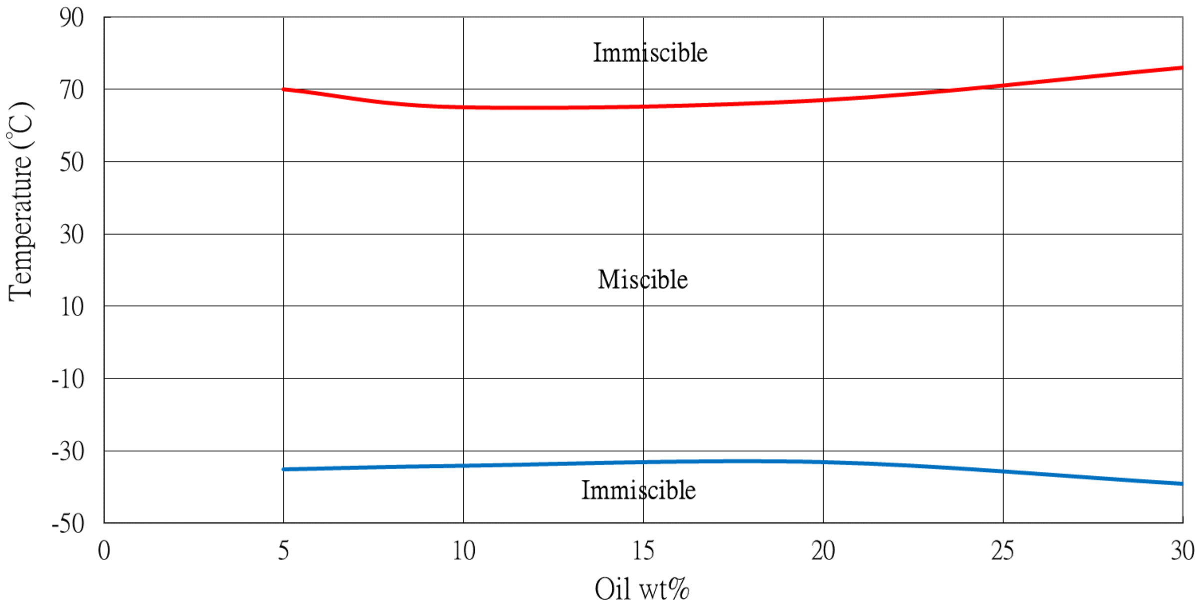

Figure 6: Miscibility chart of R1234ze-E in R1234ze (ISO-100)

4.2 Solubility and Working Viscosity of R1234ze Refrigeration Lubricants

Miscibility tendency isn't proportional related to solubility tendency in above investigation of R32 refrigeration lubricant, thus we focus on verifying whether the same situation will happen in R1234ze refrigeration lubricant or not. Based on the working condition (Sump Pressure 1114kPa, Calculating Temp. 65℃), we calculate the working viscosity in the R1234ze system and shown in Table 5. In the Figure 7, the better miscibility brings the better solubility and the working viscosity is related to the solubility.

Summarizing the refrigerant-oil test results in R32 and R1234ze, the key factor among miscibility, solubility and working viscosity is "interaction force" between oil molecules and refrigerant molecules, which is varying by different temperature and different oil-refrigerant mixture.

Table 5: Working viscosity of R1234ze refrigeration lubricants

Typical value		Mixed acid POE	R1234ze-A	R1234ze-B	R1234ze-C
Test item	unit				
Kinetic Viscosity @40℃	cSt	68	68	68	220
Miscibility, 20% oil in R1234ze	℃	<-60	-13	-32	-14
Solubility	Wt%	38.8	29	31.9	28.1
Working viscosity	cSt	1.92	3.56	4.07	7.39

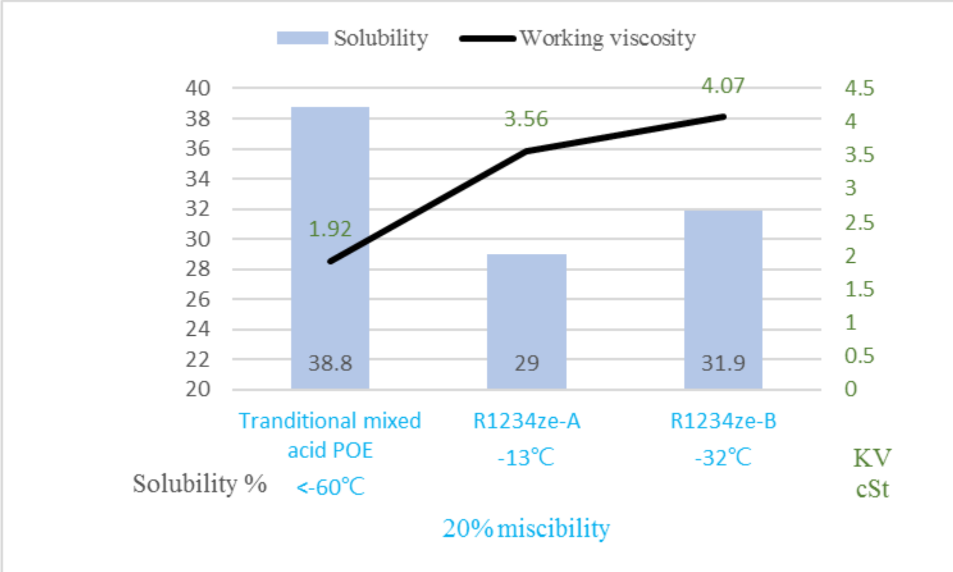

Figure 7: Miscibility, solubility and working viscosity of R1234ze refrigeration lubricants (ISO-68)

5. CONCLUSIONS

In this study we develop a series of POE refrigeration lubricants for R32 & R1234ze. We conduct some experimental tests and calculation for surface tension, lubricity, miscibility, solubility and working viscosity. Through investigation of these data, we can construct the relationship between these properties and chemical structures. Thus we find a good method for synthesis the feasible refrigeration lubricant.

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