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ABSTRACT

A New-PVE lubricant was developed for use with R32 refrigerant. R32 has been proposed as an alternative refrigerant for R410A refrigerant, to reduce global warming. In this report, we evaluated the relationship between the New-PVE lubricant and R32 and R410A refrigerants. The evaluation items were physical properties (miscibility, solubility, mixture viscosity and volumetric resistivity) and thermal stability and lubricity. In addition, a New-PVE was also developed to improve miscibility with R32 refrigerant.

1. INTRODUCTION

Today HFC refrigerants, which have an ozone depletion potential (ODP) of zero, have been used for the refrigerating equipment. Since the HFC refrigerants have a high global warming potential (GWP), the refrigerants were categorized as a greenhouse gas defined by the Kyoto Protocol in 1997, and became targets for reduction. Because of this, R1234yf, R1234yf/R32, R32, NH_3, CO_2 and R290A are being reviewed by the air-conditioning industry as R410A alternative refrigerants. (1,2) Since the GWP of R32 is 60% or more lower than the GWP of R410A and havea higher flow capacity than R410A, R32 attracts attention as one of the alternative refrigerants.

Current PVEs have inferior miscibility with R32. Because of this New-PVEs were developed by optimizing the base oil structure to improve miscibility with R32.

In this report, we evaluate New-PVE and R32 for physical properties (miscibility, solubility, mixture viscosity and volumetric resistivity), stability and lubricity.

2. EXPERIMENTAL

2.1 Lubricants & Refrigerants

The evaluated lubricants were the New-PVE and the present PVE. In addition, the viscosity grades are VG32~68. In the chemical structure of PVE shown in Figure 1, New-PVE changes the ratio of R_1 and R_2 of a side chain. The specifications of PVE and New-PVE are shown in Table 1 and Table 2. Lubricants include the antioxidant, the acid catcher, and antiwear.

Table 3 shows the evaluated refrigerants and properties of refrigerants. In addition, the difference between New-PVE and the present PVE were evaluated by miscibility, solubility, stability, and lubricity. The evaluation was performed by the method shown in 2.2~2.6 paragraph below.

2.2 Miscibility

Figure 2 shows miscibility test apparatus and method. (3) The test tube was made of the sapphire and it was filled up with lubricant/refrigerant mixture. A photo-sensor was set up to detect light through that tube. The bath temperature was gradually increased (or decreased). Initially the lubricant and refrigerant mixture was clear. As the temperature increased (or decreased), the mixture becomes cloudy which indicate lubricant / refrigerant separation. The two-phase separation temperature of that mixture was determined by the light transmittance of the photo-sensor. The temperature representing the center of this curve was the critical separation temperature (CST).

2.3 Solubility

Figure 3 shows hermetic type viscometer. This apparatus measured both the solubility and mixture viscosity of refrigerant / lubricant mixtures. (4) To measure the viscosity, a capillary-type viscometer in a pressure tight case was used. Solubility was determined by the calculating formula in Figure 3. The Daniel Chart was created on measurement data.

2.4 Volumetric Resistivity

Figure 4 shows hermetic type volumetric resistivity tester. (5) The volumetric resistivity indicate electrical insulation properties of the refrigeration lubricant. The volumetric resistivity is a ratio of electrostatic strength and the current density when the direct electric field is impressed to electrode that fills the sample. **Volumetric resistivity was measured at varied refrigerant contents (wt. %) under the below test condition*.**

*** Application voltage = 250V, Temperature = 20℃**

2.5 Stability

Stability was evaluated with the autoclave. Table 4 shows the testing conditions. The combination for an examination was PVE68/R410A, New-PVE68/R410A and New-PVE68/R32. The influence of air and wataer is also examined. The evaluated analysis items were appearance oil and catalyst, sludge, and acid value.

2.6 Lubricity

Figure 5 shows the hermetic type Block-on-Ring tester. Table 5 shows test conditions for the lubricating evaluation. The lubricants and refrigerants which were used for the examination were PVE68/R410A, New-PVE68/R410A and New-PVE68/R32. The evaluation was performed by comparison of the wear volume.

3. RESULTS AND DISCUSSIONS

3.1 Miscibility Volumetric Resistivity Test Results of PVE68/HFC410A, MO56/HCFC22

Figure 6 and 7 show the miscibility of PVE with R410A and R32. Figure 8 and 9 show the miscibility of New-PVE with R410A and R32.

The dissolution region of the current PVE and R32 became narrow compared with R410A. It was also explained that the dissolution region of those became narrow with increasing viscosity of lubricants.

Moreover, Figure 7 shows in oil content 10~20wt% PVE50 is immiscible completely and in oil content 10~25wt%PVE68 is also immiscible completely.

On the other hand, the dissolution region of the New-PVE/R410A became wide compared with present PVE/R410A. R32/New-PVE had the two-phase separation region at high temperature and low temperature side. However, the complete separation region was not seen in Figure 9. In addition, the influence of the low temperature side two-phase separation was evaluated by the system examination.

3.2 Solubility & Mixture Viscosity

Fig.10, 11 and 12 show the Daniel Chart of PVE68/R410A, New-PVE68/R410A and New-PVE68/R32. As an example, Solubility and mixture viscosity of the condition (100℃, 1.5MPa) are shown in table 6. The difference was found in mixture viscosity when New-PVE68/R410A was compared with PVE68/R410A. New-PVE68/R32 was expected that mixture viscosity becomes high because of lower solubility. However, the mixture viscosity of New-PVE68/R32 was not high because of lower viscosity of the refrigerant.

3.3 Volumetric Resistivity

Figure 13 shows volumetric resistivity of PVE68/R410A and New-PVE68/R32. PVE68 and New-PVE68 indicated $10^{11}\Omega$m range volumetric resistivity. These results show that the difference of chemical structure between PVE and New-PVE have an insignificant effect on volumetric resistivity. On the other hand, volumetric resistivity of R410A and R32 are $1.4\times10^{7}\Omega$m and $3.7\times10^{7}\Omega\cdot$m , respectively. The results show that New-PVE68/R32 shows a little higher volumetric resistivity than PVE68/R410A in the refrigerant-rich condition.

3.4 Stability

Table 7 shows autoclave tests of PVE with refrigerants. The influence on stability was not seen on two test conditions. It was understood that New-PVE is stability equivalent to the present PVE.

3.5 Lubricity

Table 8 shows lubricity of PVE with refrigerants. As for New-PVE68 and PVE68, there is little wear volume and the difference was not seen. There was no influence by the difference in the refrigerant, and lubricity was good under the examination conditions.

3.6 Improvement of miscibility

To improve the low temperature side miscibility of PVE/R32 at low temperature, New-PVE(2)s which were changed the monomer ratio of side-chain was synthesized. Table 9 shows general properties of New-PVE(2) s and Fig.14 shows miscibility of New-PVE(2)s with R32. At 15wt% of oil content, two-phase separation of New-PVE(2)68 and New-PVE(2)32 at low temperature were improved by10℃ and 20℃, respectively.
Because the basic chemical structure of New-PVE(2) is similar to New-PVE, the characteristics, except miscibility, are very close to New-PVE.
Now, we are optimizing the performance of New-PVE(2)s for customer needs.

4. CONCLUSION

The development of New-PVE changed the monomer ratio of the PVE side chain for the improvement in miscibility with R32. In addition, New-PVE was good to the solubility, mixture viscosity, stability and lubricity with R32. New-PVE can be used also for lubricant with R410A. Furthermore, New-PVE(2)s were improved the miscibility.

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(2) T. Matsumoto and M. Kaneko, M. Tamano: *The International symposium on New Refrigerants and Environmental Technology JRAIA 2010 Kobe*, 0903 (2010).
(3) JP2823123
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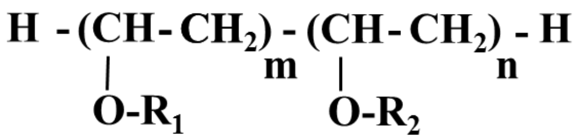

Figure 1: Chemical structure of PVE

Table 1: Specifications of PVE

	PVE68	PVE50	PVE32
Viscosity @40℃ (mm^2/s)	66.57	50.69	32.40
Viscosity @100℃ (mm^2/s)	8.037	6.790	5.120
Viscosity Index	84	84	78
Density @15℃ (g/cm^3)	0.9369	0.9315	0.9252
Acid Number, mgKOH/g	0.01>	0.01>	0.01>

Table 2: Specifications of New-PVE

	New-PVE68	New-PVE50	New-PVE32
Viscosity @40℃ (mm^2/s)	68.41	48.42	33.19
Viscosity @100℃ (mm^2/s)	8.316	6.679	5.260
Viscosity Index	88	87	84
Density @15℃ (g/cm^3)	0.9440	0.9403	0.9355
Acid Number, mgKOH/g	0.01>	0.01>	0.01>

Table 3: Properties of refrigerants

	R410A	R32
Molecular structure	CH_2F_2 / CF_3CHF_2 50 / 50	CH_2F_2
ODP	0	0
GWP	1730	675
M.W. (g/mol)	52 / 120	52
Tc (℃)	72.0	78.1
Pc (MPa)	4.95	5.78

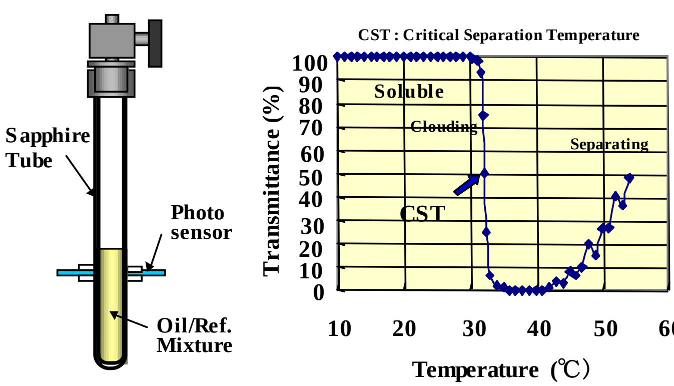

Figure 2: Miscibility test apparatus and method

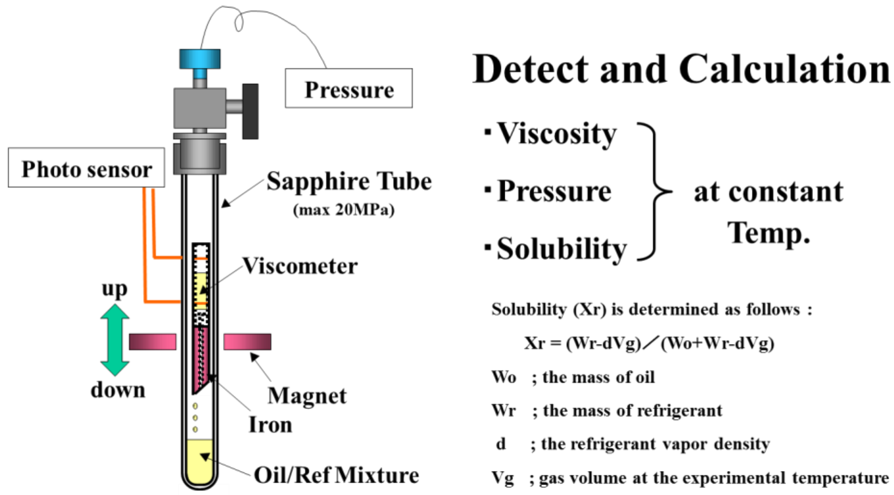

Figure 3: Hermetic type viscometer

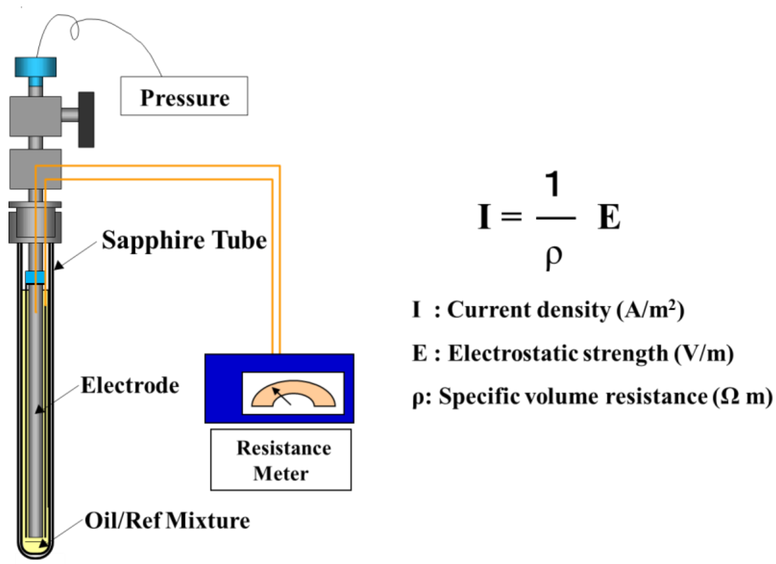

Figure 4: Hermetic type volumetric resistivity tester

Table 4: Stability test condition

Condition	Test 1	Test 2
Temperature (℃)	175	175
Test Time (day)	14	14
Oil (g)	30	30
Refrigerant (g)	30	30
Water (ppm)	50>	500
Air (Torr)	5>	100
Catalyst	Fe / Cu / Al	Fe / Cu / Al

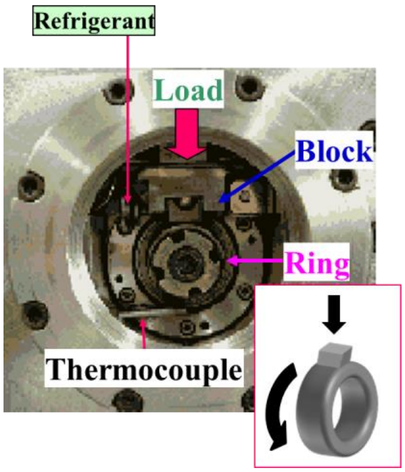

Figure 5: Hermetic Type Block-on-Ring Tester

Table 5: Wear test condition

Condition	Test 1
Temperature (℃)	100
Test Time (min)	60
Oil (g)	250
Refrigerant (MPa)	1.5
Test Piece (Ring)	FC250
Test Piece (Block)	SKH51
Load (N)	1400
Speed (rpm)	1400

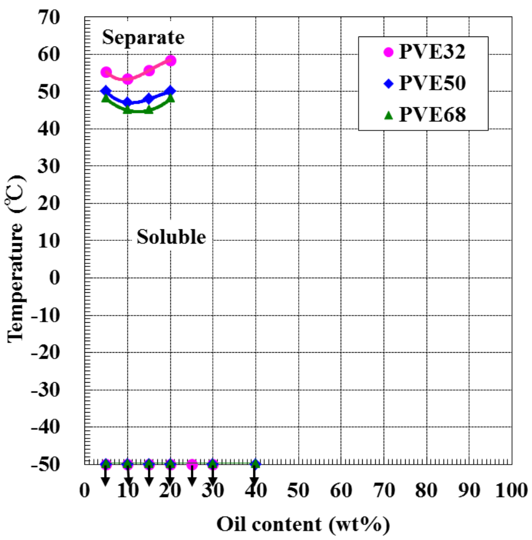

Figure 6: Miscibility of PVE with R410A

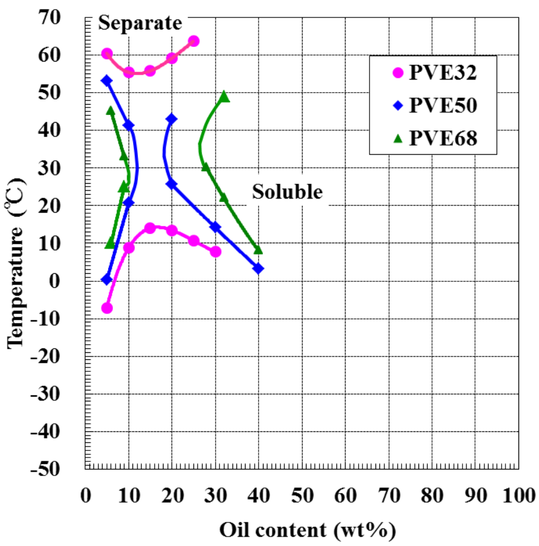

Figure 7: Miscibility of PVE with R32

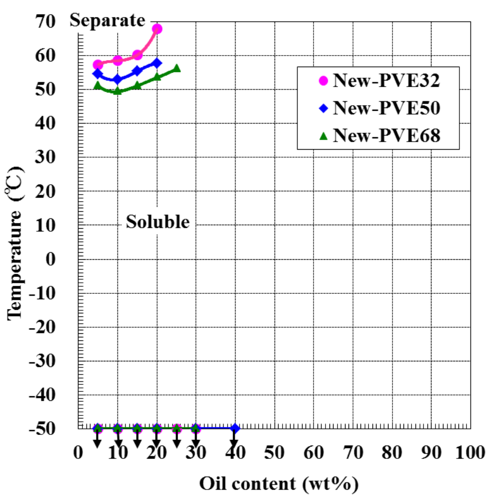

Figure 8: Miscibility of New-PVE with R410A

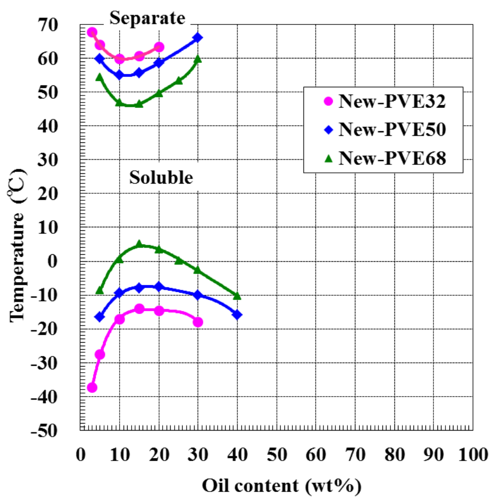

Figure 9: Miscibility of New-PVE with R32

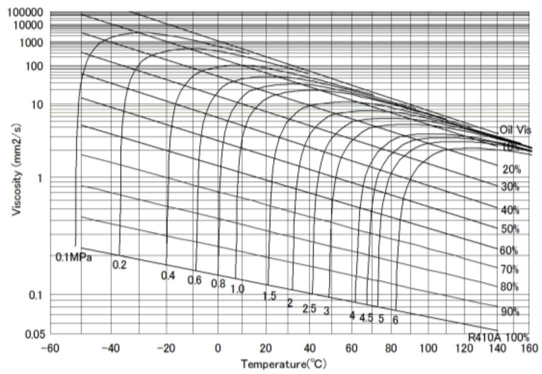

Figure 10: Daniel Chart of PVE68 with R410A

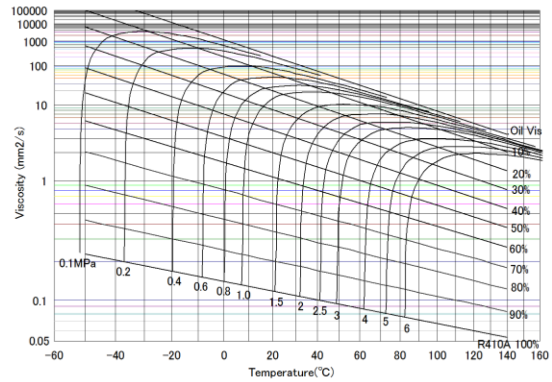

Figure 11: Daniel Chart of New-PVE68 with R410A

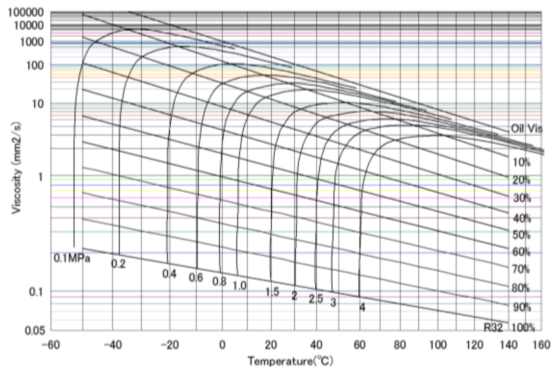

Figure 12: Daniel Chart of New-PVE68 with R32

Table 6: Solubility & Mixture Viscosity of PVE with Refrigerants (100℃, 1.5MPa)

Lubricants	Refrigerants	Solubility (wt%)	Viscosity (mm^2/s)
PVE68	R410A	4.6	5.7
New-PVE68	R410A	4.9	5.4
New-PVE68	R32	3.5	5.2

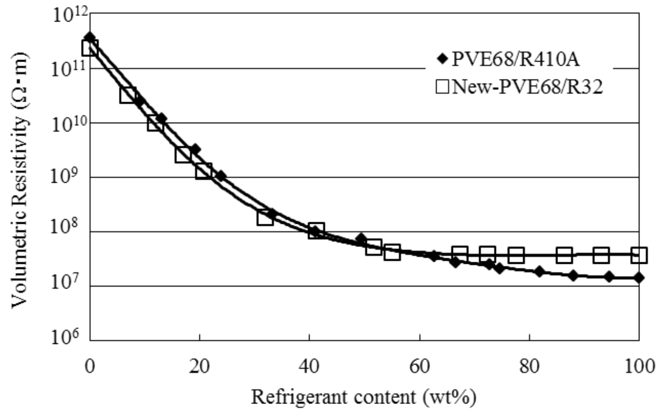

Figure 13: Volumetric resistivity of PVE with refrigerants

Table 7: Stability of PVE with Refrigerants

Test 1

Lubricants	Refrigerants	Appearance Oil	Appearance Catalyst	Acid Number (mgKOH/g)
PVE68	R410A	Good	Good	0.01
New-PVE68	R410A	Good	Good	0.01
New-PVE68	R32	Good	Good	0.01

Test 2

Lubricants	Refrigerants	Appearance Oil	Appearance Catalyst	Acid Number (mgKOH/g)
PVE68	R410A	Good	Good	0.03
New-PVE68	R410A	Good	Good	0.03
New-PVE68	R32	Good	Good	0.03

Table 8: Lubricity of PVE with Refrigerants

Lubricants	Refrigerants	Ring Wear (mg)
PVE68	R410A	1.3
New-PVE68	R410A	1.3
New-PVE68	R32	1.2

Table 9: Specifications of New-PVE(2)

	New-PVE(2)68	New-PVE(2)32
Viscosity @40℃ (mm^2/s)	65.01	28.14
Viscosity @100℃ (mm^2/s)	8.030	4.806
Viscosity Index	88	84
Density @15℃ (g/cm^3)	0.9542	0.9436
Acid Number, (mgKOH/g)	0.01>	0.01>

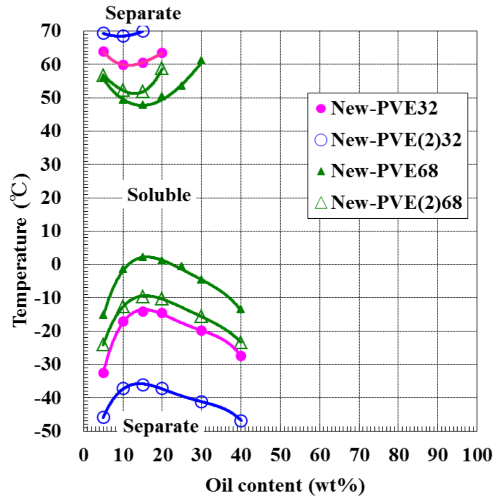

Figure 14: Miscibility of New-PVE(2) with R32