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VARIOUS PERFORMANCE OF POLYVINYLETHER (PVE) Lubricants WITH HFC REFRIGERANTS

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ABSTRACT

Polyvinylether (PVE) was introduced as innovative refrigeration oil for HFC refrigerant systems. The characteristics of PVE are non-hydrolysis nature (1), superior lubricity, solubility with process fluid and miscibility with HFC refrigerant. (1) These performances directly or indirectly contribute to the total cost down of systems. For example, most of PVE users do not use filter dryers for HFC air conditioners by controlling equilibrium water in systems to less than a few hundred-ppm (2). By confirming these advantages through numerous actual machine tests, OEMs worldwide have begun to use PVE for commercial production.

INTRODUCTION

In the early 90's, Polyalkyleneglycol(PAG) was chosen by OEMs over polyol ester(POE) for automotive air-conditioners with R134a. Since this system uses rubber hoses to connect components, moisture contamination inevitably permeates the hoses. Therefore, hydrolysis of POE was a great concern for OEMs. Also, PAG showed better lubricity than POE especially for aluminum. However, PAG could not be used in hermetic compressors, which were used for domestic refrigerators because of its relatively low electric resistivity. Since domestic refrigerators are closed systems, POE was feasible when strict moisture and contaminant control was implemented on the production line. In case of air-conditioners, most OEMs have started evaluations using POE because of the experience gained through hermetic compressors. However, hydrolysis of POE became a great concern for air- conditioners because of contamination of air and moisture during installation or repairs. Therefore, PVE, which has the same ether group as PAG, became an alternative candidate.

REFRIGERATION OIL PERFORMANCE COMPARISON

Table 1 shows an overall performance comparison between POE and PVE.

These performances were divided into two segments. One is for compressors and the other is for systems. In this table, the double circle means the performance is better than R22 systems, circle means equivalent, triangle means poor and cross means bad respectively. PVE/ HFC combination shows the same performance as R22 systems in most cases. Meanwhile, POE shows poor or bad performance in many cases such as effect of extreme pressure (EP) agent or solubility of process fluids.

LUBRICITY PERFORMANCE

PRESSURE VISCOSITY COEFFICIENT

Figure 1 shows oil film thickness under EHL region for PVE and POE. These data were measured by optical interferometry and reported by Gunsel. [(3)] Film thickness decreased significantly as refrigerant concentration increased. Meanwhile, R410A showed more reduction in film thickness than R134a. It was obvious that PVE produced thicker oil film than POE.

Pressure-viscosity coefficient, alpha values were calculated using film thickness data by a certain equation. Alpha value is the indication of oil film strength under high pressure.

Figure 2 shows the results for various oils. Naphthenic mineral oil showed highest values. PVE was next and POE was worst for each temperature. These results suggest that Mineral oil and PVE have stronger oil film under high-pressure conditions than POE. Furthermore, Yamamoto reported that PVE forms a strong solidified oil film under EHL region and protects the rubbing surface from wear. [(4)]

EFFECT OF EP(EXTREAM PRESSURE) AGENT

In order to confirm the effectiveness of EP agent, a modified four-ball test was carried out. Figure 3 shows the schematics of the apparatus and test conditions. In this test, electricity is charged between the top and bottom balls. When there is enough oil film between the top and bottom balls, electricity will not go through. When the load goes up, the top and bottom balls start to make contact with each other and electrical insulation ratio goes down.

Figure 4 shows the test results. The oils tested were Mineral Oil, PAG, POE and PVE. Three different amounts of EP agent were added in each oil. There is significant improvement by adding additives to maintain a higher insulation ratio in higher loads in the case of naphthenic mineral oil (NMO). PAG and PVE showed similar results. POE alone showed very little improvement by adding additives.

The reason for the difference in results can be explained by the polarity difference of each oil. Oil with higher polarity such as POE, can attach onto a metal surface easily and form an adsorbed oil film. However, this film is not strong enough under high temperature conditions and hinders the additives in attaching onto a metal surface.

The next test was carried out using a ball and plane-sliding tester. Figure 5 shows the schematics of the apparatus and test conditions. In this test, the upper specimen moves in a reciprocating motion. The oil temperature can be changed by the heater. These test results were reported by Yamamoto. [(4)]

Friction Coefficient was measured at different oil temperatures for POE and PVE and plotted on

Figure 6. The upper graph shows the results without TCP. POE showed lower friction coefficient under transition temperature (approximately 150 °C) than PVE. When temperature goes beyond the transition point, friction coefficient goes up remarkably as the temperature increases. Meanwhile, friction coefficient increases gradually as temperature goes up for PVE. The lower graph shows the results when TCP was added to the oils. POE showed similar results as the one without TCP. However, there is a significant improvement when TCP was added, as can be seen as friction coefficient went down for PVE above 140 °C. It is assumed that TCP broke down by heat and formed a reaction film on a rubbing surface, which resulted in reduction of friction coefficient. The profile of the surface roughness after the test proves that this reaction film helped to prevent wear.

PREVENTION OF CAPILLARY TUBE BLOCKAGE

Capillary tube blockage is the critical issue and directly related to the reliability of systems. The following are the possible causes for this phenomenon.

- High viscosity substances from process fluids such as polybutene from copper tube drawing oil, oxidation wax from rust preventive oil and silicon oil.
- Deteriorated substances of metal working fluid such as chlorine additives, sulfur additives or metallic salt.
- Deteriorated substances of Refrigeration Oil such as metallic soap due to hydrolysis of POE.
- EP Agent in Refrigeration Oil such as TCP.
- Extracted substances of organic materials such as oligomer from PET film.
- Wear powder of metals or desiccants, dust.

These factors interact with each other and result in capillary tube blockage.

The problem associated with HFC Systems is that process fluids are easily trapped in capillaries and clog them. There are two primary causes for this. One is that HFCs are immiscible with process fluids because they mostly consist of hydrocarbon types. The second is HFC refrigeration oils which are synthetic types, have poorer solubility with process fluids. This is why we have seen more capillary tube blockage for HFC/synthetic oil combination than R22 / mineral oil.

In order to compare the performance difference to prevent the capillary tube blockage between PVE and POE, we carried out an actual machine test. Table 2 shows the specification for test oil. Both of the oils contained an anti-oxidant and acid catcher. The raw materials of POE were pentaerythritol and C8, C9 branched fatty acid. PVE contained a phosphorous type EP agent (TCP) but POE did not. The total acid number of both oils was 0.01. The evaluation of capillary tube blockage was carried out using the apparatus shown in Figure 7. The compressor type was a rotary for R410A.

The mean value was calculated from the 2 test results and shown in Figure 8. The graph indicates that the POE drop in flow rate increased 5.2% with no filter dryer, while the PVE flow rate remained the same.

We also measured the total acid number (TAN), because TAN is fundamentally used as a deterioration indication of oil. The TAN of the oil after the test indicated the following results. (Figure 9)

The PVE TAN only slightly increased when tested without a dryer, while the POE TAN significantly rose to 0.2 when tested without a dryer.

Figure 10 is a photograph of the inside of the capillary tubes after the test. The capillary tube in the PVE system showed less built-up substances than that of POE. There was a tar-like black substance adhering to the walls of the capillary tube with POE even without a dryer. Prominent amounts of blue particles were observed with the POE without a dryer. We analyzed the surface substances on the walls of the capillary tube by EPMA.

Figure 11 shows the pictures after the tests with a dryer. The top-left picture in each example are the magnified surfaces of each oil. It is obvious that the PVE system has much less adherent substances than POE. The rest of the three pictures indicate element distribution for Carbon, Silicon and Iron. According to these pictures, it is obvious that the adherent substances of POE system mainly consist of Carbon and Iron. Silicones, which may be from the dryers, are mixed up with these substances.

More adherent substances were observed for non-dryer systems. (Figure 12) The carbon and iron were also main elements for POE. We found that the blue particles were copper hydroxide caused by corrosion. We assume this substance originated from the flux that was used to weld together the copper piping in the system. The reason we found more adherent substances for POE without dryer is explained by hydrolysis of POE.

These chemical equations in Figure 13 indicate the hydrolysis of POE. The starting materials of POE are carboxylic acid and alcohol. Through the chemical reaction, POE and water are produced. The problem associated with POE is this reaction is reversible. Therefore, when POE is introduced to water, it breaks down and generates carboxylic acid. This acid reacts with metals and generates metallic soap, which results in sludge or corrosion. In the case of PVE or Mineral Oil, there is no such a reaction with water.

Not only is there evidence of hydrolysis, but POE also breaks down at high temperatures at the friction area and generates metallic soap, sticky substances or solids which is related to capillary tube blockage. (Figure 14) This reaction is called tribo-chemical reaction. That is why we found carbon and iron in the adherent substance for POE system even with a dryer. In order to reproduce tribo-chemical reaction, we conducted hermetic falex test. Figure 15 shows the test conditions and apparatus. Figure 16 is the IR spectrum before and after the test. After the conclusion of the test, there was no change to the PVE. However we did observe a new peak for POE. These peaks identify the carboxylic acid that is a metallic soap.

Next, we proceeded with the same kind of test, adding process fluids in the refrigeration oil to confirm the effect of contaminants to capillary tube blockage. The test conditions are shown in figure 17. We used a conventional R22 compressor and R407C. We measured drop in flow rate across the capillary tube after 1,000 hours. Moisture was not added in this test and a dryer was not installed.

The left graph in Figure 18 shows the test results, when the piping and compressor were washed sufficiently. There was no difference in drop in flow rate between PVE and POE. The contaminants were a mixture of copper tube drawing oil, rust preventive oil, cutting oil and washing oil. 3% of the contamination for refrigeration oil was added. The reason we added excessive contaminants was to accelerate the test condition. In this test, POE showed almost twice as much drop in flow rate than PVE. Then we concluded that PVE was much more tolerant to contaminants than POE.

In order to consider the meaning of the previous tests results, we carried out the solubility test with various metal working fluids. Table 3 shows the oils used in this test. Figure 19 shows the solubility of PVE and POE with press drawing oils. The vertical line shows the precipitation temperature at which mixed liquid phase becomes cloudy and the horizontal line shows concentration ratio of press-drawing oil. The higher the solubility, the lower the precipitation temperature becomes. It is noticeable that PVE has a higher solubility with polybutene compared to POE.

Figure 20 show the solubility temperature with cutting oil and rust preventive oil. PVE has a lower precipitation temperature especially in the lower concentration area. This is a more practical condition in actual systems. In accordance with these results, we can conclude that PVE has higher solubility with process fluids than POE. We assume that solubility differences are reflected in the cap-tube blockage test results.

CONCLUSION

1. PVE has better lubricity under EHL to boundary lubrication region than POE
   - Higher pressure-viscosity coefficient
   - EP agent works more effectively
2. PVE is more tolerant to capillary tube blockage than POE.
   - No hydrolysis
   - Better solubility with process fluids
3. PVE is being used for air- conditioners mostly without filter dryers all over the world.

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(2) Fujikawa, K., Matsumoto. K., Nishikawa, T., Sato, T., Proceedings of Int. Conference Center Kobe, November 1998 p-145

(3) Gunsel, S., Pozebanchuk, M., ARTI MCLR Project No. 670-54400 April 1999

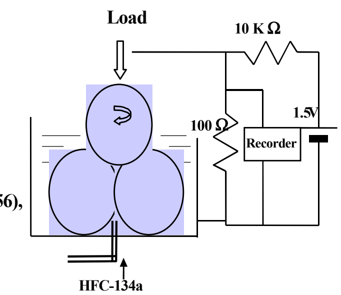
(4) Yamamoto, Y., Gondo S., and Kim, J., Proceedings of Int. Refrigeration Conference at Purdue University, July 1998 p-369

Table 1 Lubricants Performance Comparison

			POE	PVE
Compressor	Dielectric Strength & Resistivity		○	○
	Lubricity	P-V Coefficient	△	○
		Effect of EP agent	×	○
	Compatibility with various Materials		○	○
System	Cap. Tube Blockage	Hydrolytic Stability	△	○
		Tribo Chemical Reaction	△	○
		Solubility of Process Fluids	×	△
	Elimination of Filter Dryer		△	○
	Miscibility with HFC Refrigerant		○	⊙

Base Line = M.O./HCFC22
⊙: Better ○: Equivalent △: Poor ×: Bad

- Test Conditions
  - Revolutions : 500 ppm
  - Oil Temp. : 50°C
  - Load : 0.02 Mpa every 3min.
  - Refrigerant : R134a, 5ltr./min.
  - Lubricants : M.O.(VG56), POE,PVE(VG68)



* Electrical Insulation Ratio = Measured Voltage / Added Voltage(15mv) ~ 100 %

Fig. 3 Electrically Isolated 4-Ball Tester

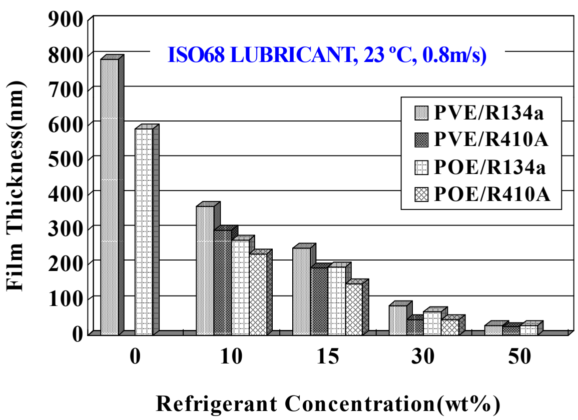


Fig. 1 Film Thickness for R134a and R410A

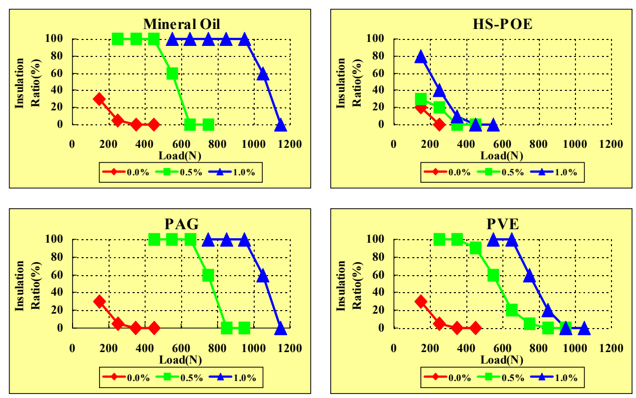


Fig. 4 Effect of EP agent

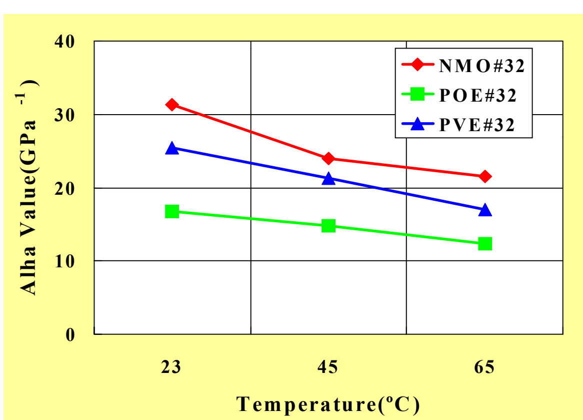


Fig. 2 Pressure-Viscosity Coefficient

•Frequency : 500 cycle/min
•Amplitude : 2.5 mm
•Load : 50 N to 200 N
•Pmax : 1.11 to 1.76 Gpa
•Atmosphere : R134a
•Material : Bearing Steel

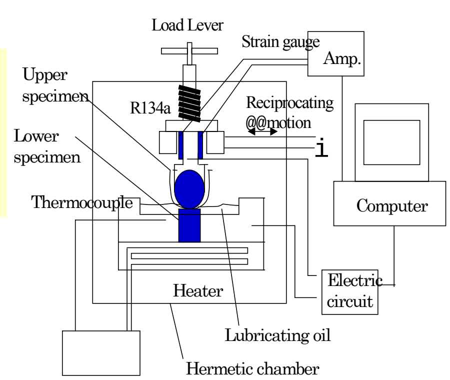


Fig. 5 Ball and Plane Sliding Tester

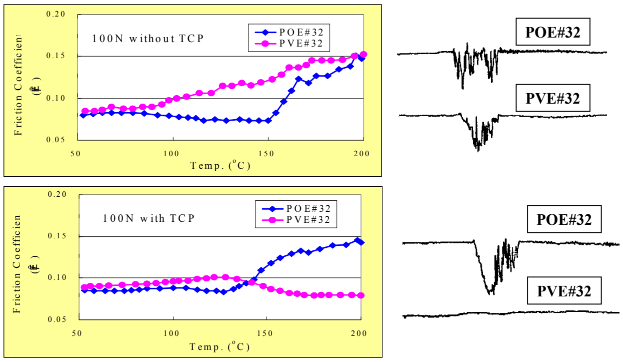


Fig. 6 Effect of EP agent to Friction Coefficient

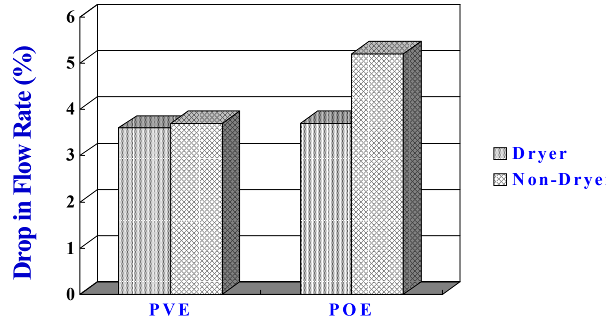


Fig. 8 Test Results

Table 2 Specification of Test Oils

Item	PVE (VG68)	FB-POE (VG68)
Viscosity 40°C mm^2/s	63.1	68.9
Viscosity 100°C mm^2/s	7.8	8.4
Viscosity Index	84	89
Density @15°C g/cm^3	0.938	0.960
T.A.N [mgKOH/g]	0.01>	0.01
Color	L0.5	L0.5
, o	811	0

FB-POE:iC8/iC9(50:50)PE
+DBPC+EPOXIDE

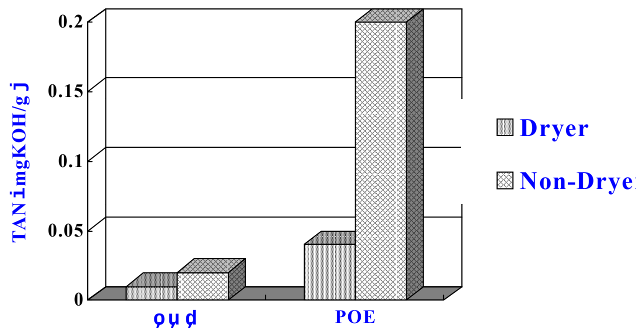
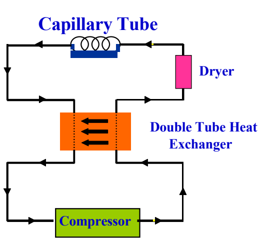


Fig. 9 Oil Analysis after the Test



Scheme of Short Circuit Capillary Tube Blockage Test Apparatus

Short Circuit Test Conditions

Compressor	Rotary Type for R410A
Refrigerant	R410A
Capillary Tube	ϕ 1.00mm~ 2m
Pd	3.33 M p a
Ps	0.4 M p a
Td	110 °C
Ts	30 °C
Temperature of Capillary Tube	-5 °C
Revolutions	4500rpm
Operation Time	1,500 hrsD

Fig. 7 Test Conditions(1)

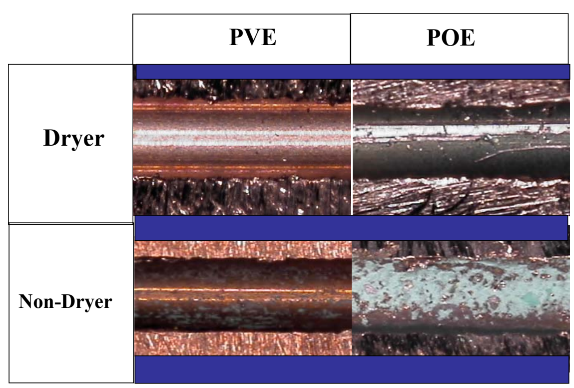


Fig. 10 Inside of Capillary Tubes

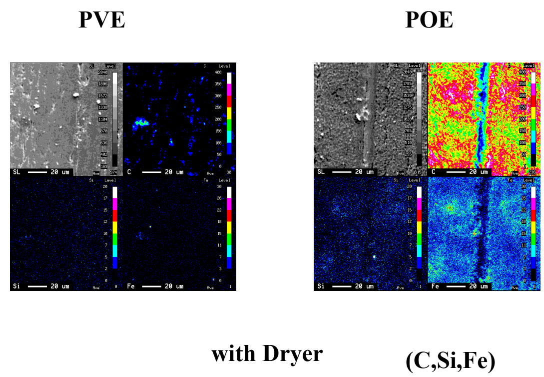


Fig. 11 Surface Analysis of Capillary Tube(1)

- Friction areaF

Boundary Lubrication AreaiApprox.300 • j

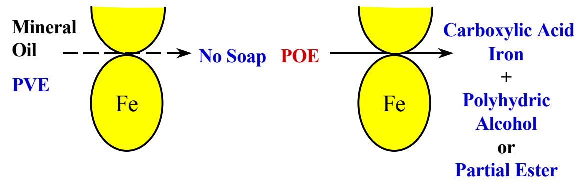


Fig. 14 Tribo Chemical Reaction

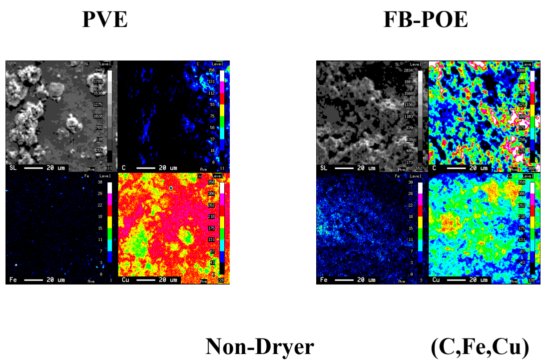


Fig. 12 Surface Analysis of Capillary Tube(2)

- **Test Condition**
  - Load : 224 N
  - Revolution : 290 rpm
  - Atmosphere : R134a
  - Pressure : 0.3 MPa
  - Oil : POE, PVE

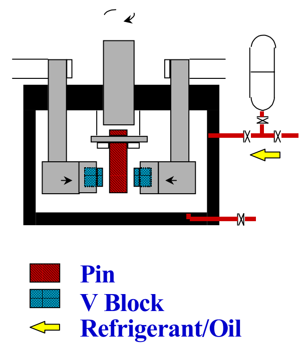


Fig. 15 Hermetic FALEX Test

- **Ester is made from Acid and Alcohol**

RCOOH + R'OH ⇄ RCOOR' + H2O

Carboxylic Acid　Alcohol　Ester　Water

- **Hydrolysis causes Metallic Soap**

RCOOR' + H2O → RCOOH + R'OH

FeO + 2 RCOOH → Fe(OCOR)2

Carboxylic Acid Iron

- **PVE & M.O. → No Reaction with Water**

Fig. 13 Hydrolysis of POE

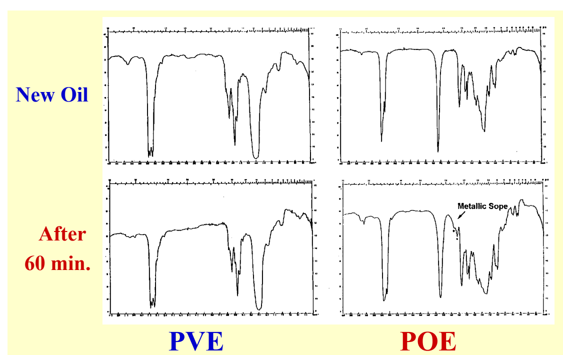
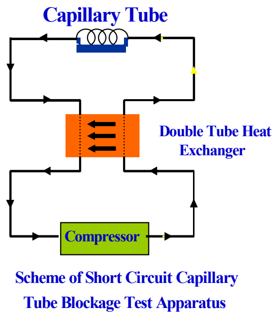


Fig. 16 IR Chart after FALEX Test



Short Circuit Test Condition

Compressor	Rotary Type for R22
Refrigerant	R407C
Capillary Tube	ϕ 0.65mm~ 2m
Pd	2.45 Mpa
Ps	0.2 Mpa
Td	100 ℃
Ts	25 ℃
Temperature of Capillary Tube	-20 ℃

Fig. 17 Test conditions(2)

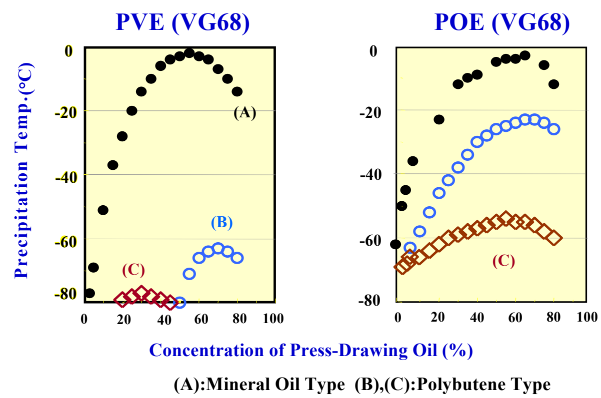
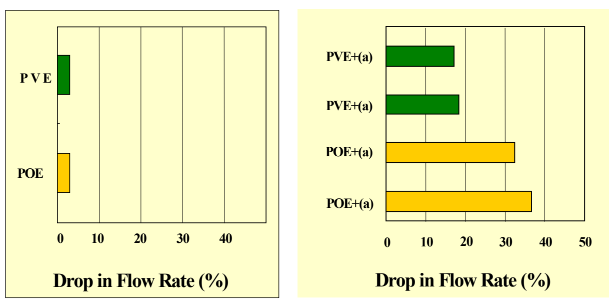


Fig. 19 Solubility of PVE with Process Fluids(1)



(a) F Contaminant (Drawing Oil C Rust Preventive Oil C Cutting Oil C Washing Oil)

Fig. 18 Test Results(Drop in Flow Rate)

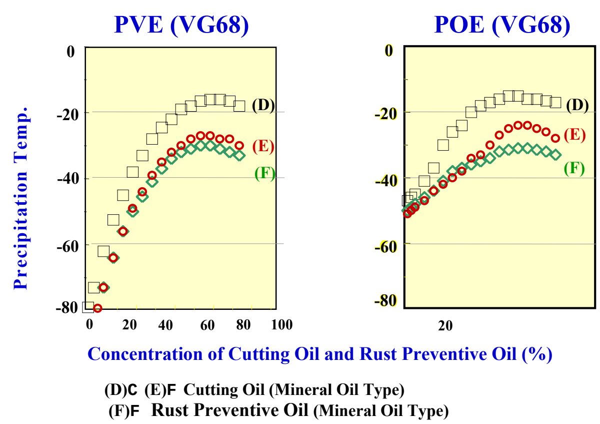


Fig. 20 Solubility of PVE with Process Fluids(2)

Table 3 Solubility with Metal Working Fluids

	Base Oil	Oil Name	Viscosity @40℃(mm_2/sec)
Press Drawing Oil	Mineral Oil	(A)	280
	Polybutene	(B)	120
		(C)	300
Cutting Oil	Mineral Oil	(D)	20
		(E)	20
Rust Preventive Oil	Mineral Oil	(F)	15