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S. Tominaga  
_Idemitsu Kosan Co._

M. Takagi  
_Idemitsu Kosan Co._

M. Takesue  
_Idemitsu Kosan Co._

T. Tazaki  
_Idemitsu Kosan Co._

M. Goodin  
_Apollo America Corporation_

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PRACTICAL STABILITY PERFORMANCE OF POLYVINYLETHER (PVE) WITH HFC REFRIGERANTS

Shoichi Tominaga, Minoru Takagi
Lubricants Department, Idemitsu Kosan Co., Ltd. Tokyo Japan
(E-mail: 49002320@si.idemitsu.co.jp)
Masahiko Takesue, Toshinori Tazaki
Lubricants Research and Development Laboratory, Idemitsu Kosan Co., Ltd.
Mark Goodin
Apollo America Corporation, Southfield, MI
(E-mail: mgoodin@apolloamerica.com)

ABSTRACT

Deterioration degree of PVE Lubricants was investigated by analyzing used oils after various compressor and system tests with HFC refrigerants. As a result, deterioration of PVE itself was not observed and long term reliability was confirmed. Furthermore, autoclave tests with water and air were performed to determine the reliability limit of PVE in comparison with mineral oil and polyolester. Through these studies, it was confirmed that PVE with HFC refrigerant has enough tolerance to air or water contamination to secure long term reliability.

INTRODUCTION

PVE was introduced as an innovative refrigeration oil for HFC refrigerant systems. The characteristics of PVE were reported many times in the past. Among these, non-hydrolysis nature (1), solubility with process fluid (2), oil film strength in EHD region (3), effectiveness of antiwear additive (4) and miscibility with HFC refrigerant (5) were the key characteristics looked at by OEMs who chose PVE. 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 less than a few hundred ppm (6). By confirming these advantages through numerous actual machine tests, OEMs worldwide have begun to use PVE for commercial product applications. In this report, we gathered the used oil analysis data after the above mentioned machine tests to determine the practical stability performance of PVE.
TEST METHOD AND CONDITIONS

Because of the many number of samples, PVE VG 68 (PVE68) with antioxidant, acid catcher and antiwear additive was chosen as the candidate oil to be analyzed. In addition to this oil, naphthenic mineral oil VG56 (MO56) and fully branched polyolester VG68 (POE68) were used in autoclave testing as a reference. Table 1 shows the general specifications for each oil.

Among the numerous durability tests conducted with PVE 68 by using actual compressors and systems, a total of 183 samples were analyzed. The lubricant samples analyzed were taken from either in the middle of the test or after the test. The test conditions varied from normal operating conditions to accelerated life test conditions. OEM’s have created accelerated life test conditions depending upon scope and purpose. Some of these tests were performed with contaminants such as rust preventive oil or cutting oil premising insufficient washing process of compressor parts. Others were performed with water or air premising insufficient air or water removal when these systems would be installed or repaired. Most of refrigerants used in these tests were either R407C or R410A. Some of them used R404A for commercial refrigeration application. The compressor types were mainly rotary and scroll, with many not using filter dryers.

Reliability limits of PVE68 were evaluated by autoclave testing under more severe conditions. The PVE results were compared to the results of MO56 and POE68. Figure 1 shows autoclave testing apparatus

<table>
<thead>
<tr>
<th>Factors</th>
<th>Test Conditions</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>10 torr</td>
<td>Practical operation</td>
</tr>
<tr>
<td></td>
<td>200 torr</td>
<td>Air contamination</td>
</tr>
<tr>
<td></td>
<td>760 torr</td>
<td>Abnormal condition</td>
</tr>
<tr>
<td>Water</td>
<td>50 ppm</td>
<td>Practical operation</td>
</tr>
<tr>
<td></td>
<td>500 ppm</td>
<td>Water contamination</td>
</tr>
<tr>
<td></td>
<td>1,000 ppm</td>
<td>Abnormal condition</td>
</tr>
</tbody>
</table>

Table 1 General Specification of Each Oil

<table>
<thead>
<tr>
<th>Additives</th>
<th>PVE68</th>
<th>MO56</th>
<th>POE68</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (mm²/s @ 40°C)</td>
<td>64.2</td>
<td>54.9</td>
<td>60.2</td>
</tr>
<tr>
<td>Viscosity (mm²/s @ 100°C)</td>
<td>7.67</td>
<td>5.96</td>
<td>7.68</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>77</td>
<td>12</td>
<td>88</td>
</tr>
<tr>
<td>Density (g/cm³ @ 15°C)</td>
<td>0.926</td>
<td>0.918</td>
<td>0.960</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-40</td>
<td>-35</td>
<td>-35</td>
</tr>
<tr>
<td>Total Acid Number (mgKOH/g)</td>
<td>0.01&gt;</td>
<td>0.01&gt;</td>
<td>0.01</td>
</tr>
<tr>
<td>Volumetric Resistivity (Ω·cm, RT)</td>
<td>1.6+14</td>
<td>8.6+14</td>
<td>8.6+13</td>
</tr>
<tr>
<td>Additives</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Antioxidant</td>
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<td>Antioxidant</td>
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<td>Antioxidant</td>
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<tr>
<td>Acid catcher</td>
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<td>Acid catcher</td>
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<td>Acid catcher</td>
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</tbody>
</table>
and Table 2 shows the test conditions. In these studies, R410A refrigerant was used for PVE68 / POE68 and R22 refrigerant was used for MO56 testing.

TEST RESULTS AND ANALYSIS

Endurance Test Results

Figure 2 shows the relationship between test duration and Total Acid Number (TAN) for 183 samples. Even after long term operation, the overall TAN increase is minimal for PVE68 and considered having superior stability in an actual machine. Among these data, some showed significant TAN increases in a relatively short period of the test time and chlorine, sulfur, potassium or barium were detected. Since these substances are not contained in the original oil and well known as additives used in rust preventive or cutting oils, it was determined that these lubricant samples came from test systems that experienced insufficient washing processes or contaminants were intentionally added to make the test condition more severe.

In order to investigate precisely the stability performance of PVE68, the relationship between test duration and consumption of each additive were studied.

Figure 3 shows the consumption ratio for a phosphorous type antiwear additive. Most of the samples showed more than 80% of remaining ratio, which is considered sufficient enough to ensure long term effectiveness of antiwear performance at a rubbing surface.

Next we studied the consumption ratio of antioxidant which results were plotted on Figure 4. Most of the samples showed more than 60% remaining ratio. A few samples operated in systems for more than 4,000 hours showed much lower remaining ratios. Therefore, we studied the relationship between the antioxidant consumption ratio and TAN increases for the samples that operated for a duration of 4,000 hours or more. Figure 5 shows the results. Since TAN increase was not observed, it was concluded that no
deterioration of PVE base oil occurred even for the samples that showed lower antioxidant ratios.

Furthermore, Figure 6 shows the same kind of relationship for the acid catcher. The purpose of this additive is to neutralize the acidic substances which are introduced into the system by contaminants or generated by deterioration of contaminants, additives or refrigeration oil itself. It also reacts with water and reduces the water content in systems. Unlike other additives, there is no clear relation between duration and residual contents. Sometimes it was consumed relatively early and other times it remained sufficiently after a long duration. We assume the cause of this data fluctuation is that the acid catcher reacted with water or contaminants in the system in relatively early stage of the operation and reacted with deteriorated substances later. Therefore, when amount of water or contaminants are high, it reacts with these substances and is consumed rapidly.

In this way, the additives in PVE68 reacted effectively with oxygen, acidic substances and water in the oil and prevented the base oil from deterioration.

**Autoclave Test**

Since deterioration of PVE68 was not observed through endurance tests, autoclave test were performed to confirm the reliability limit of PVE68 under more severe conditions. Naphthenic mineral oil which has been used as a refrigeration oil for R22 and polyolester which is used with HFC refrigerant were also evaluated as a reference.

In order to clarify the effect of air and water contamination, the test conditions listed on Table 2 were
chosen. These tests represent a normal operating condition, very severe conditions in practical operation and abnormal operating conditions.

Figure 7 shows the effect of air contamination. In these studies, test conditions were fixed at 175 °C for 30 days and water was controlled at less than 50 ppm. At this point, vacuum ratio was less than 10 torr and considered no air in the autoclave. Air was added in the autoclave by controlling vacuum ratio at 200 and 760 torr respectively. 760 torr vacuum ratio means no refrigerants but only air and oil in the autoclave. All oils showed significant TAN increase at 760 torr, while TAN increase was relatively small at less than 50 torr and 200 torr for all three oils and considered to be in an acceptable range. In general, POE has better anti-oxidation performance than PVE or mineral oil, however the test results showed otherwise especially when the vacuum ratio was 760 torr. This is assumed to be because a certain amount of water in air reacted with POE and caused hydrolysis.

Although, air contamination is considered to cause oxidation of oil over long term operation, it is confirmed that PVE68 has enough tolerance to a practical amount of air contamination and no worse than a mineral oil/R22 combination.

Next, the effect of water contamination was studied by carrying out the autoclave tests with different water contents. Again, test conditions were fixed at 175 °C for 30 days. Water contents in sample oils were controlled at less than 50 ppm, 500 ppm and 1,000 ppm for all three oils. Air was removed by vacuum pump at room temperature for 5 minutes. Figure 8 shows the test results. None of the oils showed TAN increase at less than 50 ppm. POE68 alone showed significant TAN increase at 500 and 1,000 ppm content of water.

It has previously been reported many times that Polyolester will hydrolyze under certain conditions and Polyvinylether will not hydrolyze because of its ether structure. This can be reconfirmed through this study.

The TAN increase for PVE68 at 1,000 ppm of water was assumed to be caused by hydrolysis of

![Fig. 7 Effect of Air Contamination (175°C, 30 days, No Water, Catalyst:Fe, Cu, Al)](image)

![Fig. 8 Effect of Water Contamination (175°C, 30 days, No Air, Catalyst:Fe, Cu, Al)](image)
antiwear additive. According to these results, it was concluded that PVE68 has sufficient stability with water at least in a practical usage range.

CONCLUSION

• Numerous PVE oil samples after endurance tests were analyzed. Most of them showed minimal TAN increase and considered to be sufficient to guarantee long term reliability.
• Enough antiwear additives in PVE remained even after long duration.
• Although a few samples showed low antioxidant remaining ratio after long duration, it was confirmed that these samples did not show TAN increase and no deterioration of base oil.
• The remaining ratio of the acid catcher varied. This may be caused by fluctuation of amount of initial water and contaminants in systems.
• The autoclave test results suggest that PVE with HFC refrigerant has enough tolerance to air or water contamination even compared to a conventional mineral oil/R22 combination.

REFERENCES

(1)(5) Kaneko, M., Tominaga, S., Goodin, M., ASHRAE Seattle, WA, 1999
(3) Gunsel, S., Pozebanchuk, M., ARTI MCLR Project No. 670-54400 April 1999
(6) Fujikawa, K., Matsumoto. K., Nishikawa, T., Sato, T., Proceedings of Int. Conference Center Kobe, November 1998 p-145