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Abstract

The stability and durability of POE refrigeration lubes are discussed. Hydrolytic stability tests by the autoclave method were conducted at different temperatures with hydrolytically stable POE (HSPOE, fully branched POE). The life of the HSPOE was estimated from the Arrhenius plot. An oiliness agent was selected as an antiwear additive from antiwear tests on a tribometer and from compressor durability tests with high side rotary compressors. In addition to lubricity, insulation properties in hermetic motors are also needed for refrigeration lubes for hermetic compressors. The volume resistivity and relative permittivity of the mixture of POE and HFCs were measured, and it was confirmed that the mixture had insulation properties equivalent to those of a mixture of mineral oil and HCFC-22. It was shown that the moisture was effective for the resistivity of POE and HFC mixture.

Introduction

In Japan, new air conditioners with R407C and R410A have been on the market since 1997, with mainly POEs applied as the refrigeration lubes. Small air conditioners mainly use rotary compressors. As the operating conditions for refrigeration lubes in rotary compressors are very severe and the stability of the refrigeration lube affects the life of the total system, it is very important to determine the life of the refrigeration lube under various operating conditions. Optimization of the chemical structures of POEs has been reported, but the deterioration of POEs at various temperatures and periods has not been studied well. It is well known that POE lubes are chemically very stable against HFC refrigerants, but a weak point of POEs is hydrolytic deterioration. Hydrolytic stability tests are generally conducted in bomb tests using autoclaves under refrigerant atmosphere. Hydrolytic stability tests have been done at different temperatures. The total acid numbers (TAN) of refrigeration lubes were measured and the reaction rates were determined. By transferring the TAN and temperature into an Arrhenius plot, the period at which the TAN reaches a certain number at a certain temperature can be predicted. Because refrigeration lube also serve as insulating fluids in hermetic motors, insulating properties are needed as well. The dielectric properties (i.e., volume resistivity, permittivity, etc.) of lubricant and refrigerant mixtures have not been reported yet. In this paper, the stability of POEs is reported, and the dielectric properties, advantages and disadvantages of additives, and the results of compressor durability tests are described.

Experiments

Hydrolytic stability tests

A fully branched POE (H8B9B[1], ISO VG 68) with a phenol type oxidation inhibitor and epoxide type stabilizer was used in serial evaluations. 500 ppm moisture was added to the sample oil just before the evaluation, and 50 g of sample oil was poured into an autoclave with a capacity of 200 ml. One piece each of steel, copper, and aluminum plate (50 × 6 × 0.5 mm) was added as catalysts. The autoclaves were capped and sealed, the vessels were cooled in a dry ice and alcohol bath, and the interiors of the vessels were evacuated by a vacuum pump. Then 20 g of R407C or R410A was introduced into the autoclaves. After aging in electric ovens at certain temperatures for certain periods, the autoclaves were opened and the sample oils were filtered under vacuum conditions in order to degas the refrigerant. After the treatment, the TAN of the samples was measured.

Tests for insulating properties

An autoclave with a capacity of 500 ml and an electric cell inside that is specified by JIS

C 2101 was used for the evaluation of the insulating properties of POE (H8B9B) with HFCs. A certain amount of oil was poured into the autoclave, and after evacuation by a vacuum pump, a certain amount of R407C or R410A was introduced into the vessel. The total amount of the oil and refrigerant mixture was 200 g. Based on the procedure of JIS C 2101, the volume resistivity was measured at room temperature. The resistivity of the mixture of 20 mass % H8B9B and 80 mass % R410A with a small amount of organic acid (2-ethyl hexanoic acid, reagent) or water (ion exchanged) was measured as well. The relative permittivity of the oil itself and of the oil and refrigerant mixture (20 mass % of H8B9B and 80 mass % of R410A) was also measured using the same testing device based on JIS C 2101.

Friction and wear test

A tribometer[1)] was used to evaluate the lubricity of oil and refrigerant mixtures under high pressure and temperature. The vane and disk type specimens were set inside a high pressure chamber, and the upper shaft was rotated. The tests were conducted under HFC atmosphere using specimens consisting of steel vanes (SKH, high speed tool steels) and iron disks (FC, cast iron) and of steel vanes (SKH) and aluminum disks (A390). After the test, the amount of wear to the vane nose and disk surface was measured. POE (H8B9B) was used as the base oil, and a phosphate type extreme pressure additive and ester type oiliness additive were evaluated.

Compressor durability tests

Compressor durability tests were conducted for 2000 hours with simplified gas circuits employing currently used 1 HP vertical single piston R22 compressors. R407C was used as a refrigerant and POE (H8B9B) with and without antiwear additive was tested as the refrigeration lube. The current mineral oil containing antiwear additive with R22 and ABs containing antiwear additive with R407C was also tested. The discharge pressure was set at 2.85 MPa, and the suction pressure was controlled to 0.379 MPa. The discharge temperature was around 100 degrees C. The ambient temperature was room temperature, and the return gas temperature was between 6 and 17 degrees C. The discharged gas was cooled by water. After passing through the desiccant, XH11, the refrigerant was expanded by an expansion valve and the refrigerant gas was returned to a compressor. The compressors were disassembled after the durability tests and the wear conditions at the bearing parts (i.e., vanes, rollers, shafts, bearings, etc.) were observed.

Results and discussion

Hydrolytic stability tests

The hydrolytic stability test results are shown in Table 1. Although organic fatty acids generated by decomposition occasionally have a reaction catalyst effect, the hydrolytic reactions were treated as first order reactions because the added moisture was only 500 ppm and the reaction was limited in the beginning stage. Since the increase in the TAN in these tests was mainly due to the hydrolytic reaction, the TAN was defined as representing k, the degradation reaction rate constant. The log TAN is plotted on the Arrhenius diagram relative to the reciprocal of the absolute temperature. The plots fit onto linear lines for each period. Then the Arrhenius diagram is transferred to the diagram shown in Figure 2, which indicates the relationship between the duration and temperature. The periods at which the total acid number reaches a certain number can be estimated from this diagram. When the POE is exposed at 120 degrees C as bulk temperature with R410A and 500 ppm moisture, the time to reach TAN 0.05 mgKOH/g will be 20,000 hours, 50,000 hours for TAN 0.2, and 100,000 hours for TAN 1.0. As the bulk temperature of lubes in compressors is kept lower than 100 degrees C on average, the duration period of HSPOE will be longer than 100,000 hours if the upper limit of the TAN of POEs is determined to be 0.2 mgKOH/g.

Insulating properties

The results are shown in Table 2 and Figure 3. Since the volume resistivities of both new lubes and HFC refrigerants are lower than those for current mineral oil and R22, the electric current loss in the compressor is a cause of concern. In this diagram, although the liquid refrigerant concentrate deteriorates the resistivity, the POE and HFC mixture maintains almost the same level as the current combination at 10 mass % of oil concentration or higher. R410A increased in its relative permittivity. The influence of added contaminants on the resistivity is shown in Figure 4. Moisture was more effective for the resistivity of the POE and R410A mixture than was the organic fatty acid that is an element of H8B9B.

Table 1 Hydrolytic stability test results

Temperature ℃ (1/T)	150 (2.364E-3)		175 (2.232E-3)		200 (2.114E-3)		225 (2.008E-3)	
Period hr	TAN	log (TAN)	TAN	log (TAN)	TAN	log (TAN)	TAN	log (TAN)
500	0. 01	-2.000	0.04	-1.398	0.13	-0.886	0.75	-0.125
1000	0.00	-	0.01	-2.000	0.41	-0.387	1.37	0.137
2000	0.01	-2.000	0.38	-0.420	0.90	-0.046	-	-
4000	0.11	-0.959	0.88	-0.056	2.64	0.422	-	-

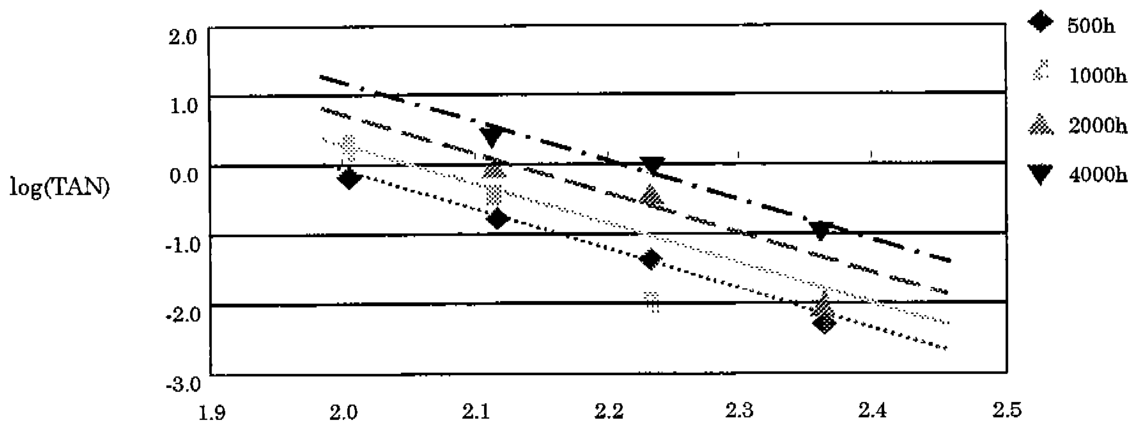

Figure 1 Arrhenius plot from hydrolytic stability tests

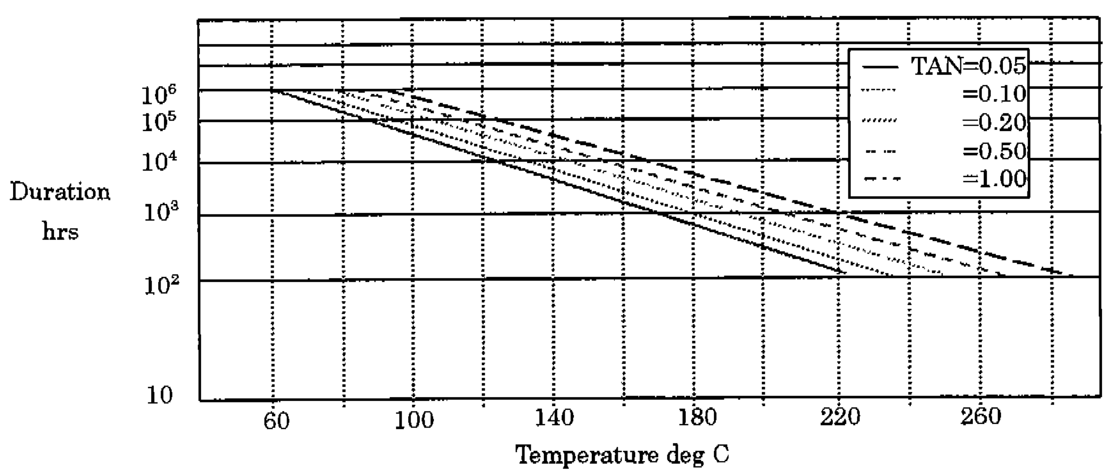

Figure 2 Relation between temperature and duration of POE

Table 2: Test conditions for insulating properties

Property	Oil	Ref.	Refrigerant/Oil mass %					
			100/0	95/5	90/10	80/20	50/50	0/100
Resistivity ρ, Ωcm	POE H8B9B	R407C	7.5*10^{10}	1.2*10^{10}	1.4*10^{10}	1.4*10^{10}	5.3*10^{10}	4.2*10^{14}
		R410A	8.2*10^{10}	-	1.3*10^{10}	1.4*10^{10}	4.8*10^{11}	4.2*10^{14}
		R134a	7.2*10^{11}	6.3*10^{10}	2.5*10^{10}	4.1*10^{10}	7.4*10^{10}	4.2*10^{14}
	Mineral Oil	R22	8.0*10^{11}	1.1*10^{11}	9.9*10^{9}	3.6*10^{10}	7.6*10^{10}	7.8*10^{14}
Permitivity ε	POE H8B9B	R410A	0.465	-	-	5.20	-	3.09

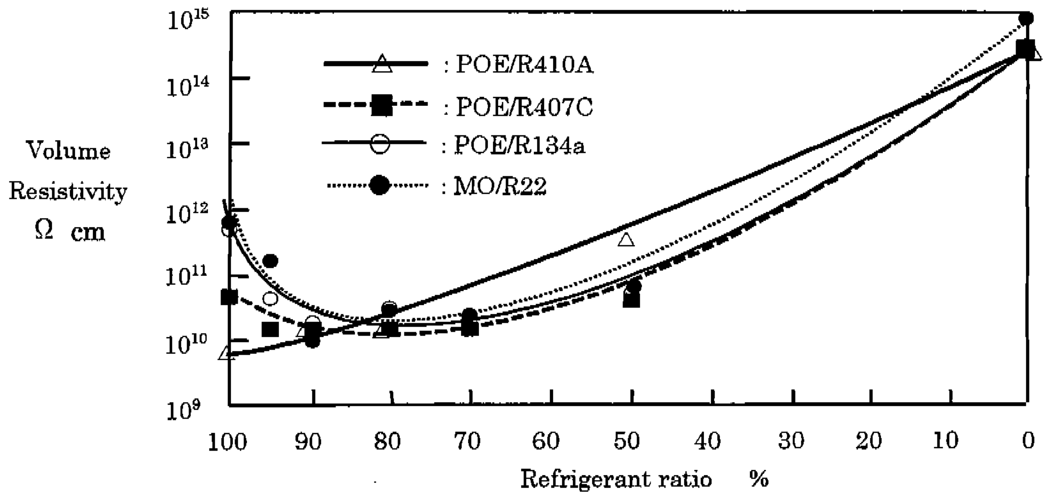

Figure 3 Volume Resistivity of POE and HFC mixture

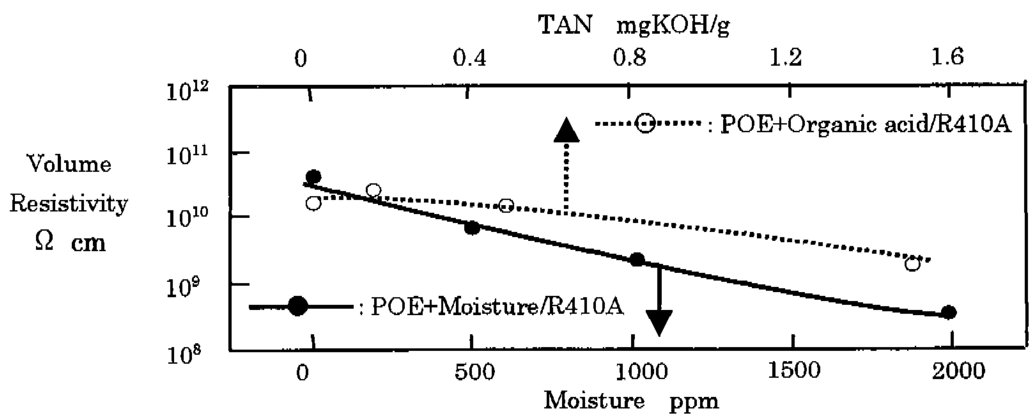

Figure 4 Deterioration of resistivity with contaminants

Friction and wear tests

The test results are shown in Table 3. Phosphate type additives that affect the moderate extreme pressure by chemical reaction worked effectively with the steel and iron specimen. The wear amount decreased as the phosphate dosage increased. Although the oiliness agent was shown to be effective as well, it was inferior to phosphate when used at the same dosage.

Between the steel and aluminum specimen, phosphate degraded the lubricity. The oiliness agent improved the lubricity and decreased the amount of wear to the aluminum surface. Phosphates react with the steel surface but sometimes increase the friction coefficient. For lubrication between steel and aluminum, phosphate was thought to increase the friction, increase the surface temperature, and then weaken the lubricating oil film.

Table 3 Effect of additives

Vane/Disk	Base stock	Phosphate mass%	Oiliness agent mass %	Wear to vane Width, μm	Wear to disk Height, μm
Steel/Iron	H8B9B	None	None	306	1.8
		0.5	None	272	1.5
		1.0	None	229	1.0
		3.0	None	188	0.5
		None	1.0	241	2.5
Steel/Aluminum	H8B9B	None	None	299	9.0
		1.0	None	405	10.7
		None	1.0	244	4.3

The working mechanism of phosphates is believed to be as shown below.

- Phosphates adhere to the steel surface.
- Phosphates form acid phosphates.
- The acid phosphates react with the steel surface and form ferrous organic salts.
- The salts react and form ferrous phosphates.
- The ferrous phosphates reduce the extreme pressure.

In polar bases like POEs, since the intermediate ferrous organic acids are stabilized due to solvation, ferrous phosphate cannot be produced so easily. This is the reason why such phosphates do not work well in polar bases. The analysis results for sludge in the capillary tubes recovered from durability tests of air conditioners are shown in Table 4.

Table 4 Sludge in capillary tubes

Refrigerant	Base	Additive	Sludge
R407C/R410A	(HS)POE	Phosphate	Organic metal salt Organic salt Ferrous phosphate Ferrous organic phosphate
R22	Mineral Oil	Phosphate	Ferrous chloride/Copper chloride Wear particle Organic materials Sulfuric compounds Ferrous phosphate
HFCs	Alkylbenzene	Phosphate	None

Ferrous organic phosphates produce insoluble sludge by self degradation and precipitate inside capillary tubes. As HFCs are very polar, organic salts like ferrous organic phosphates and organic metal salts are rejected from the lube and HFC solution. Since they are bulky and sticky, the sludge decreases the capillary flow rate. Although ferrous phosphate or metal chlorides are found inside the capillary tubes, a significant flow rate drop is not found because the sludge is not bulky or sticky in the current HCFC systems. Based on these results, physical adhesion type oiliness agents are preferable for HFC applications compared with extreme pressure additives that induce chemical reactions.

Compressor durability tests

In the compressor durability tests, ABs with phosphate showed the best results for the surface roughness of the vanes and rollers[2]. H8B9B without antiwear additives showed better surface roughness compared with the current mineral oil and R22 combination. POE with phosphate made the worse results even for the steel vane and iron roller combination in spite of the test results on the tribometer. The reason is assumed to be that the phosphate additive increased the friction coefficient and caused stick slip phenomena between the vane and roller.

Table 5 Compressor durability test results

Oil		Compressor analysis		Oil analysis			
Oil VG	Phosphate additive	Ra μm vane/roller New	Ra μm vane/roller 2000h	Viscosity mm^2/s @ 40 deg. C	TAN mgKOH/g	Color ASTM	Contaminant mg/100g oil
POE 68 N	No	0.15/0.22	0.48/0.48	61.3	0.00	L1.5	17
POE 68 Y	Yes	0.15/0.22	1.04/1.88	64.9	0.07	L2.5	4
ABs	Yes	0.15/0.22	(0.44/0.40)*	-	(0.00)*	-	(7)*
MO 38	Yes	0.15/0.22	0.94/0.97	38.2	0.00	L1.5	49

*( )=Average for ABs

Phase separation temperature

Miscibility was also measured with both R407C and R410A based on JIS K 2211. Even with a higher viscosity like VG 68, H8B9B is more miscible than naphthenic mineral oil and white oil, so good oil return is expected even with long pipelines.

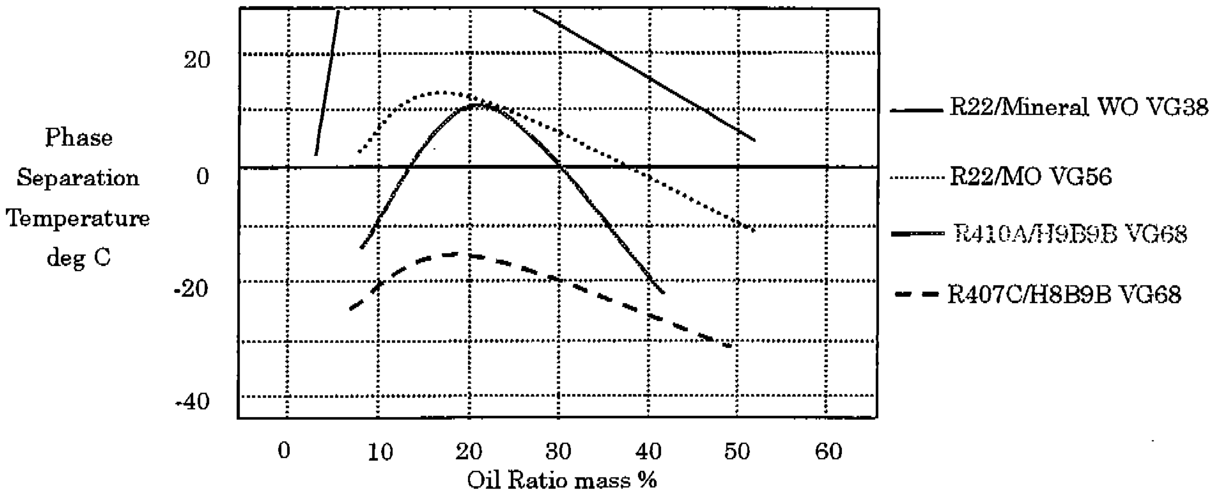

Figure 5 Phase separation temperature

Summary

Wider applications of HSPOE for air conditioners have been studied. Hydrolytic stability tests were conducted at between 150 and 225 degrees C for between 500 and 4000 hours with R407C and R410A. By transferring the TAN and temperature into an Arrhenius plot, the period at which the TAN reaches a certain number at a certain temperature can be predicted in order to estimate the life of HSPOE.

The use of antiwear additives was studied. Oiliness agents were expected to moderate the friction between steel and aluminum. Considering the mechanisms of sludge formation in the capillary tubes, phosphate type extreme pressure additives cannot be recommended.

The insulating properties of the mixture of POE and HFCs were evaluated, and it was proved that the mixtures have equivalent properties to the mixture of the current mineral oil and R22.

References

1) Sunami, M., Takigawa, K., Suda, S.: Proc., Int. Refrigeration Conf., Purdue (1994) 153.

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