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Refrigeration Lubricant Based on Polyolester for Use With HFCs and Prospect of its Application With R-22 (Part 2) Hydrolytic Stability and Compressor Endurance Test Results

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REFRIGERATION LUBRICANT BASED ON POLYOLESTER FOR USE WITH HFCS AND PROSPECT OF ITS APPLICATION WITH R-22 (PART 2) HYDROLYTIC STABILITY AND COMPRESSOR ENDURANCE TEST RESULTS

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ABSTRACT

Application of HFC refrigerants for air conditioners and refrigerators has been studied. Development of a common oil, based on a combination of polyolester and additive packages, is aimed for R-22 and HFCs refrigerants, and the evaluation tests of reliability in compressor and refrigeration system brought about good results. This refrigeration lubricant is already partly commercialized in HFC refrigerants and the application for R-22 is now under development.

INTRODUCTION

Recently protection of the earth circumstance against the ozone layer destruction and global warming has become a challenge for the world. As the measures for this point, the total abolition of CFC refrigerants in 1995 and start of regulation on HCFC refrigerants from 1996 with aim of abolition in principle in the year of 2020 has been agreed upon. Therefore, HFC refrigerants have been noted as the alternative refrigerants. R-134a is expected to substitute for R-12, meanwhile R-404A and R-407C for R-22. Polyolester(POE) has been developed as the refrigeration lubricant applicable for both commercial refrigerants of R-22 and the expected HFC refrigerants.

Part 1 report is mainly dealing with the testing result of tribology, and Part 2 with stability of base oil, effect of additives and testing result of hydrolytic stability by use of moisture absorbent as element test, and endurance test result of compressor, reliability test result in refrigeration system and the related practical situation as reliable test.

ELEMENT TESTS

Hydrolytic stability

Principal physical properties as a refrigeration lubricant are miscibility with refrigerant, high electrical insulating property, high lubricity and thermal and chemical stability. POE is the most suitable in HFC refrigerants though having a fear of oil deterioration and material corrosion by the unique hydrolytic reaction of POE (eq. (1)).

$$RCOOR' + H_2O \rightarrow RCOOH + R'OH \quad \text{------ (1)}$$

First, a stability test was made by using an autoclave testing device for the purpose of grasping the hydrolytic properties due to the difference in molecular structure of POE. Study on α-branched acid rich POE (A32) as the base oil showed that the increase in total acid number(TAN) was lower and more stable than that of α-branched acid free POE (N32) in Fig. 1. From this result, α-branched acid rich POE(A32) was selected as the base oil and thereafter various tests were made by using POE(A32) unless it is specified.

As one of the methods to further improve the hydrolytic stability, the epoxy type additive was added. Two types of additives, L-A and L-B, were evaluated under the same condition as shown in Fig. 2. Figure 2 shows that thermal stability and hydrolytic stability as refrigeration lubricant could be enhanced by the addition of epoxide L-B to POE (A32). From above results, the optimal composition of epoxy type additive (L-B), antiwear additives (Part 1: AP and S-P) and other additives has been studied in the case of base oil POE(A32). (Refer to table 1)

Thermal stability

Thermal stability testing was made to study the possibility of application of the selected POE-C to both HFC refrigerants and R-22. As a thermal stability evaluation method, the sealed glass tube test including a very small amount of air and water was carried out at a temperature of 175℃ for 21 days. It was observed that there were neither discoloration in any cases due to oil deterioration nor occurrence of sludge. No corrosion of metal piece of Fe, Al, Cu was also observed in the sealed glass tube. The results under severer temperature condition of 200℃ together with the above results are shown in Table 2. It is clear that the application of POE-C with HFC refrigerants and R-22 can be expected with adequate thermal stability.

Moisture removal effect

When moisture exists in refrigerant, there is a possibility of hydrolytic reaction for POE as described in eq. (1). For the application as a refrigeration lubricant in the refrigeration units, it is necessary to maintain the concentration of moisture and total acid number(TAN) of oil at a certain level. For these purposes, a moisture absorbent (zeolite) was introduced into a refrigeration units, its effect was evaluated by the measurement of the moisture absorbing rate through the elementary test. Figure 4 shows the measurement results of lapse change of moisture contents in oil by circulating POE-C including water and antiwear additive (AP and S-P) in a closed system, which is an oil circulation tester as shown in Fig. 3. Figure 4 shows that moisture was absorbed rapidly after the start of test and was diminished down to hundreds ppm after 50 hours, resulting in almost a saturated level of moisture concentration.

Moisture absorbing ratio is modelized and overall mass-transfer coefficient (K_{fav}) can be calculated with the following equation.

$$C_n = C_o\,[\mathrm{exc}\,(-K_{fav}\,Z/u)]^n \quad \text{---------}\ (2)$$

C_n : Moisture content at outlet of absorbing tower
C_o : Moisture content at inlet of absorbing tower
Z : Length of absorbing tower
u : Liquid space velocity
n : Exponent

The overall mass transfer coefficient (K_{fav}) was 8 sec^{-1} based on the result of Fig. 4. By use of these experiment results, the trend of moisture concentration is calculated in the case of refrigeration unit with moisture absorbent. When moisture trend is calculated using the assumed condition of table 3 and K_{fav}= 8sec^{-1} resulting from the elementary test, moisture content reduces rapidly after the operation started and becomes a few ppm at 300 hours later because of moisture absorbent. Consequently it will be possible to decrease the moisture concentration in the oil and restrict the hydrolytic reaction by the selection of optimum absorbent and its optimum amount. That is, when moisture absorbing rate is presumed to be greater enough by compared with hydrolytic reaction and moisture mass transfer rate in the system is faster, reaction rate of equation (1) is regarded as chemical reaction rate controlling by hydrolysis. When the amount of oil in the unit is larger enough than that of the moisture, reaction rate (γ_A) is shown as the following equation (3).

$$-\gamma_A = K_1 \cdot C_{RCOOR'} \cdot C_{H_2O} \quad \text{----------}(3)$$

γ_A : Rate of reaction
K_1 : Rate constant
$C_{RCOOR'}$: Oil concentration in system
C_{H_2O} : Moisture concentration in system

If the moisture concentration with moisture absorbent is one tenth of that without moisture absorbent, the hydrolytic reaction rate becomes one tenth, too.

Figure 5 shows the measurement result of the absorbing rate of antiwear additives. The trend of absorbing amount of S-P additives to the moisture absorbent becomes constant after 20 hours later, when the total amount of additive absorbed was 20 %. Therefore, the optimum additive amount or additive concentration to be added can be calculated by anticipation of absorbing amount of antiwear additives S-P to the moisture absorbent.

RELIABILITY TESTS

Endurance test of compressor

Endurance acceleration test is one of the methods to study the applications of new refrigeration lubricant. The compressed high temperature refrigerant gas is circulated using the bypass line as shown in Fig. 6. In this endurance test, a rotary compressor was used and the exit pressure of compressor was fixed at a high value, 1.5 times of the normal one. The results is shown in Fig. 7. From Fig. 7, it is obvious that the optimum POE-C with both of HFC refrigerants (R-134a, R- 407C, R-404A) and R-22 achieved endurance time target of 2000 hours, but POE-D with all refrigerants was hard to succeed in the target time. It has been proved from the above results of Part 2 as well as the tribology test results of Part 1 that POE-C is more suitable and can be prospected at the same application for HFCs and R-22 refrigerants.

Endurance test of refrigeration system

After execution of endurance test of refrigeration system charged with R-404A and POE-C, the physical properties were measured. The result show that, by use of a moisture absorbent, the moisture concentration in lubricant was rapidly down to less than 100ppm after the initial stage, and the total acid number was less than 0.05mgKOH/g even after 15,000 hours, being very stable. Also, general physical properties of oil (viscosity, ASTM color) have little change and the concentration of antiwear additives S-P was keeping at a diminishing rate of about 20 % equivalent to that of initial absorbing rate at the time of element test.

On the other hand, when tested without moisture absorbent to refrigeration system, the moisture concentration had little decrease from the initial value (about 400ppm) and total acid number rose from 0.01mgKOH/g to 0.15mg KOH/g after the lapse of 12,000 hours(Refer to Fig.8). From the above results, hydrolytic stability determined by moisture concentration reduction seems efficient by use of moisture absorbent, and hydrolytic reaction stability is thought to be adequate for the refrigerator using POE-C by application of the optimum moisture absorbent.

Practical use of POE

Refrigeration system for R-134a using POE-C has been run under practical use in the Marine Transport Refrigeration Unit for 4 years and more than 10,000 units are under good operation conditions up to now all over the world, without serious troubles at all due to POE-C. Figure 9 shows the variations of moisture concentration in oil and total acid number at the time of accelerating endurance test of the Marine Transport Refrigeration Unit.

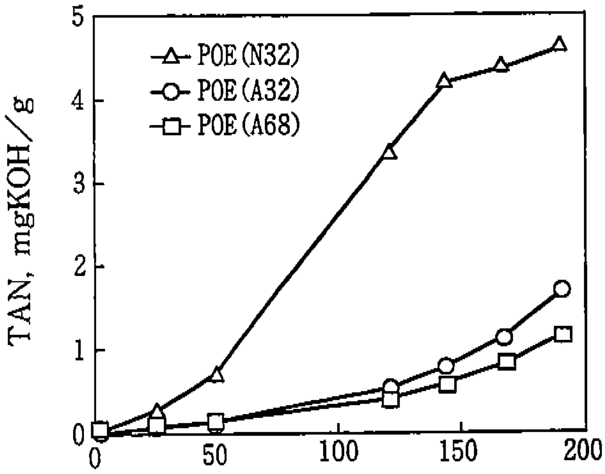
CONCLUSIONS

On the bases of selection of base oil, additive effect and moisture removal effect, POE-C has been developed as refrigeration lubricant for the practical use with HFCs and R-22 refrigerants.

(1) α -branched acid rich polyolester is the most suitable in HFCs and R-22 refrigerants.

(2) The optimal composition of epoxy type additive, antiwear additives (aryl phosphate and sulfur-phosphous) and other additives has been studied in the case of α -branched acid rich polyolester.

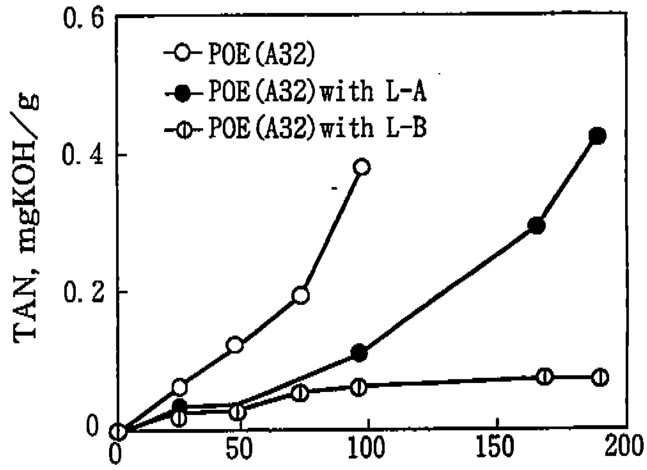
(3) Hydrolytic reaction stability is thought to be adequate for refrigerator using POE-C by application of the optimum moisture absorbent.



N : α − branched acid free
A : α − branched acid rich
Figure indicates ISO viscosity grade

Fig.1 Influence of chemical structure of POE on hydrolytic stability

(Temp : 175℃
Gas pres : 300kPa
Moister conc. : 1000ppm)



L − A : Epoxide A
L − B : Epoxide B

Fig.2 Effect of epoxide on hydrolytic stability

(Temp : 175℃
Gas pres : 300kPa
Moister conc. : 1000ppm)

Table.1 Compositions of formulated oils

Polyolester	POE − C	POE − D
Base oil	POE (A32)	POE (N32)
Additive		
AO[1]	○	○
Epoxide (L-B)	○	○
AP[2]	○	○
S − P[3]	○	○

1) Antioxidant
2) Aryl phosphate
3) Sulfur − phosphorus type additive

Table.2 Thermal stability of POE – C

Refrigerants	R – 134a	R – 404A	R – 22
175℃ × 21days			
Appearance	Colorless and Clear	←	←
ASTM Color	< 0.5	←	←
Sludge	None	←	←
200℃ × 21days			
Appearance	Colorless and Clear	←	←
ASTM Color	< 0.5	←	←
Sludge	None	←	←

(Another contents ; Metal (Fe, Aℓ, Cu), a little air and water)

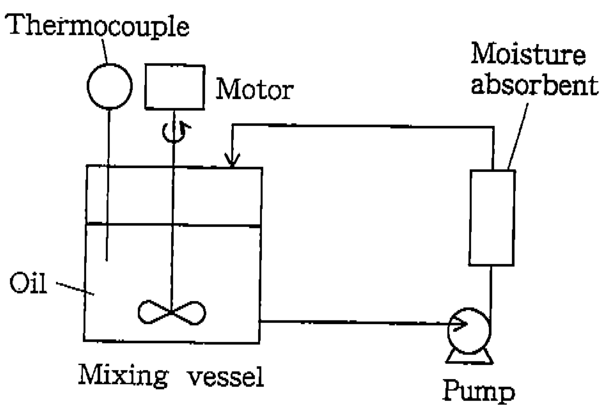


Fig.3 Oil circulation tester
(Zeolite ; 30g, Oil flow rate ; 0.3 ℓ/min, POE charge ; 1400g)

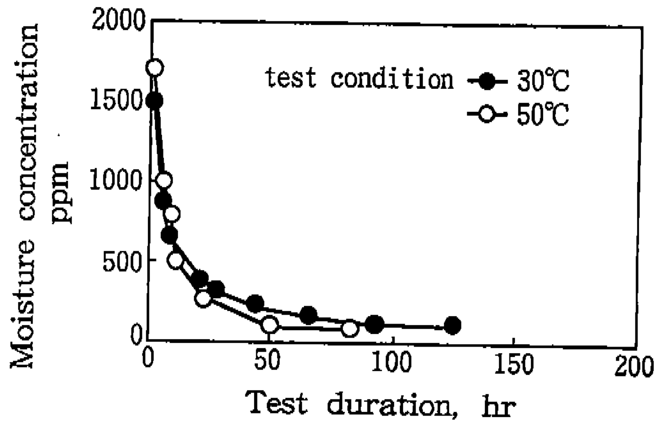


Fig.4 Change in moisture concentration with test duration.
(Initial moisture conc. ; 1500~1700ppm)

Table.3 Example of air conditioners

Air conditioner	Cooling capacity 15kW
Refrigerant	Initial moisture concentration : 100ppm
POE	Initial moisture concentration : 1000ppm
Moisture absorbent	Zeolite : 90g

(Ref. charge : 5kg, POE charge : 1.5 ℓ)

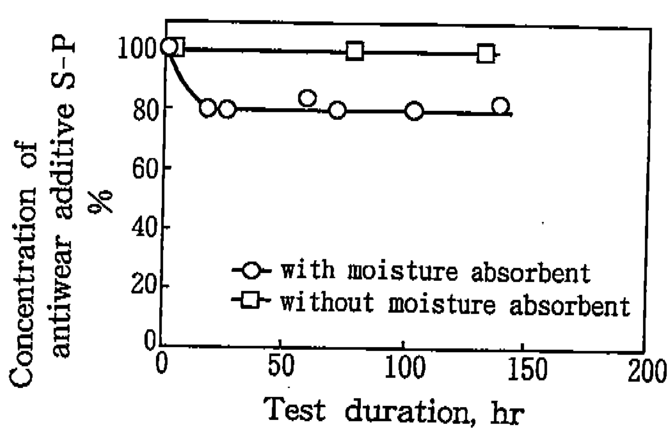


Fig.5 change in concentration of antiwear additive S – P
(Temp. : 30℃, Zeolite : 30g)

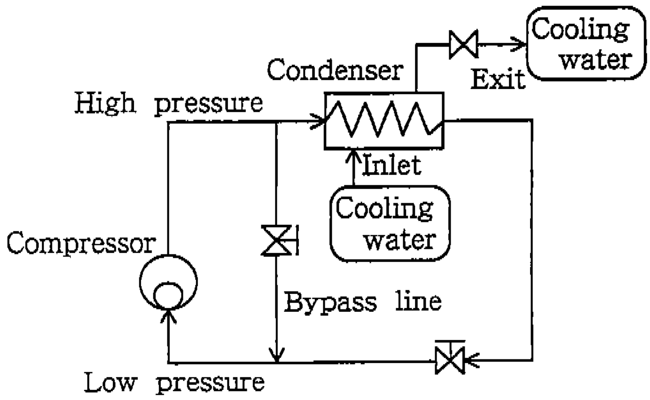


Fig.6 Endurance acceleration test flow of compressor
(Comp. : Rotary type, Cooling capa. ; 4.5kW, Displacement : 28cc/rev)

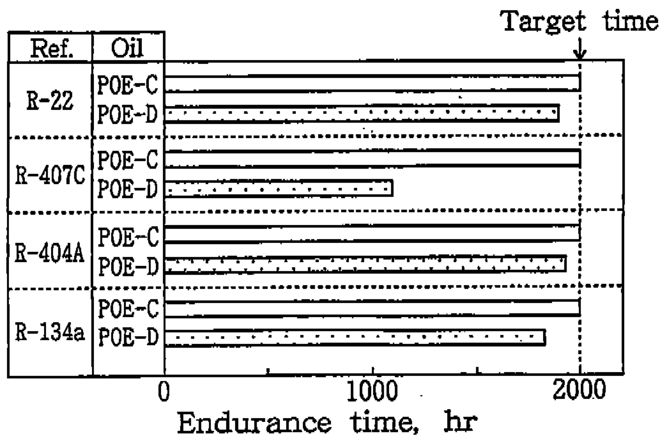
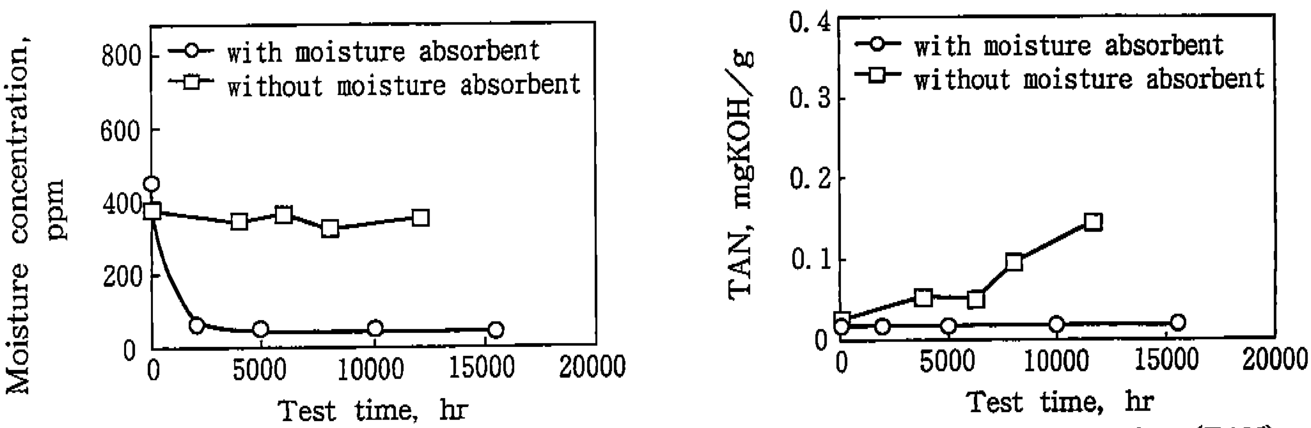


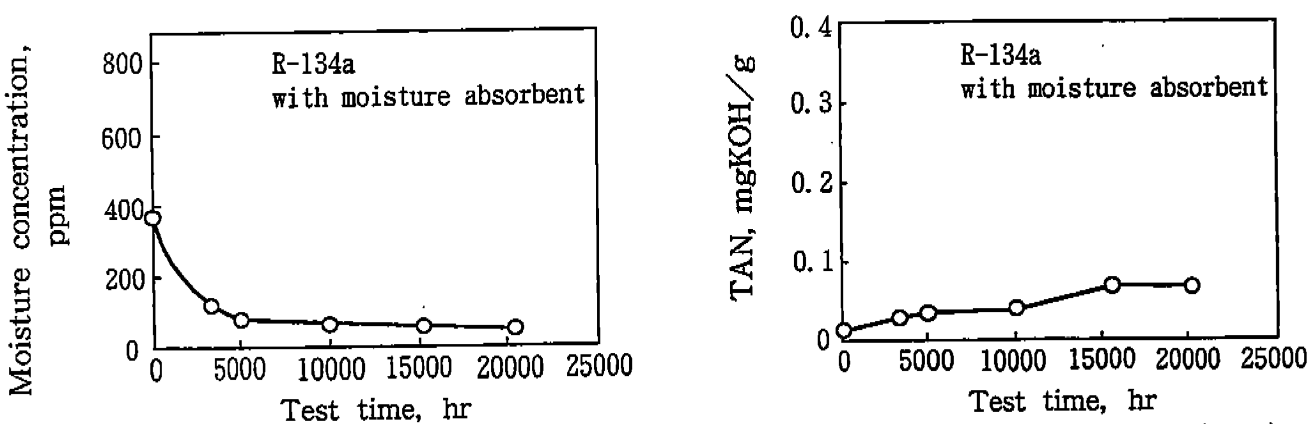
Fig.7 High load acceleration test duration of compressor
(Ref. charge : 800g, POE charge : 800cc)



(a) Change of moisture concentration

(b) Change of total acid number (TAN)

Fig.8 Influence of moisture absorbent in the refrigerator.
(Comp. : Scroll type, Cooling capa. ; 15kW, Discharge temp. ; 100~110℃)



(a) Change of moisture concentration

(b) Change of total acid number (TAN)

Fig.9 Physical property change of POE in the Marine Transport Refrigeration Unit.
(Comp. ; Scroll type, Cooling capa. ; 7kW, Discharge temp. ; 120℃)