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A NEW SYNTHETIC HYBRID REFRIGERATION OIL FOR R410A AND R407C

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ABSTRACT

There is a need to improve conventional polyolester lubricants that are currently being evaluated as the optimal refrigeration base oil for the alternative refrigerants R410A and R407C, which are expected to be designated as the replacement of HCFC 22. Prior studies show that the conventional polyolesters and other lubricants have poor hydrolysis and solubility.

This paper is an introduction to a new hybrid polyolester made by a simple synthesis of alcohols, olefins and carbon monoxide as raw materials, and it's evaluation process as a refrigeration oil as compared to conventional lubricants. Having a 100% alpha branched structure with a wide temperature miscibility range, research on this hybrid polyolester shows excellent hydrolytical, oxidation and chemical stability and lubricity not seen in esters introduced in the past.

INTRODUCTION

The production of air conditioners using either R407C or R410A as a replacement refrigerant to HCFC-22 has now begun. In the majority of cases, HS-POE (High Stability-Polyol Ester) is used as a refrigeration oil where HFC type refrigerants are used in refrigerators and air conditioning units. However, the current HS-POE is not necessarily satisfying the quality or cost requirements, so an oil with higher quality and lower cost is being researched.

We have focused on the synthesizing procedures of POE. As a result, using a different synthesizing procedure from the normal process, HB-SL (Hybrid Synthetic Lubricant) having a 100% alpha branched structure (quaternary carbon atom) was successfully developed.

ESTERIFICATION METHODS & MOLECULAR STRUCTURE

In general, POE is synthesized by an internal dehydration of polyhydric alcohols and monobasic acid(Eq.1). Currently in Japan, a high viscosity HS-POE (VG68) for HFC air conditioners is synthesized by PE(pentaerythritol) with i-C_8 acid(2-ethyl hexanoic acid) and i-C_9 acid(3,5,5-tri methyl hexanoic acid). After the two different types of fatty acid are synthesized, the esterification process follows.

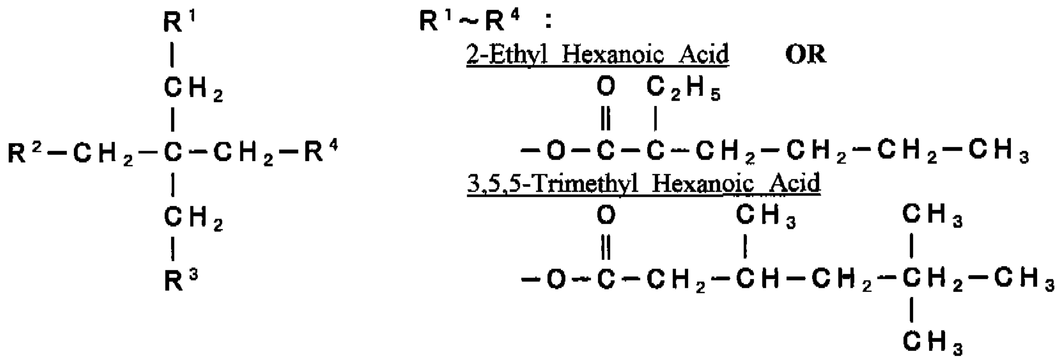
Eq. 1: HS-POE Process

Olefin + CO → Monobasic acid

Polyhydric alcohol + Monobasic acids → HS-POE

The molecular structure of a high viscosity HS-POE (VG68) is shown in Eq. 2. The alpha carbon atom is attached to an ethyl group and hydrogen atom or in some cases, two hydrogen atoms are bonded. This HS-POE results into mixtures of five different types of molecules.

Eq. 2: HS-POE molecular structure



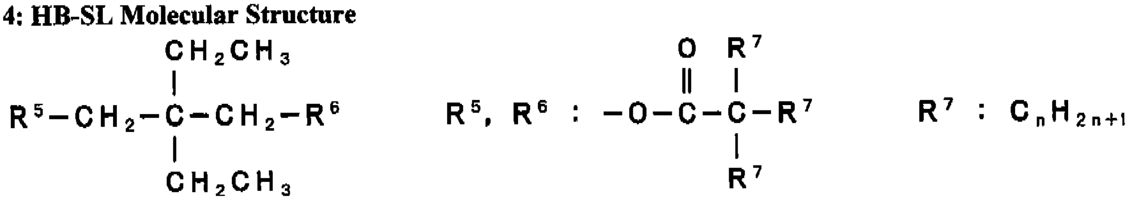
As in contrast, HB-SL is synthesized from alcohol, olefin and CO (carbon monoxide) (Eq.3) by a single process. In addition, since fatty acids are not used as a raw material, there are no supply limitations as in the case of HS-POE. As a result, a stable HB-SL of a 100% alpha branched structure is made and when compared to HS-POE, the HB-SL is improved in hydrolytic stability and mutual miscibility with HFC refrigerants.

Eq. 3: HB-SL Process(Reference:1)

NPG + Olefin + CO → HB-SL

HB-SL has a structure of tertiary fatty acid bonding to NPG (neopenthyl glycol)(Eq.4). From this advanced synthetic method, HB-SL has mixtures of over 10 different types of molecules and has a wide range in molecular weight as seen also in mineral oils.

Eq. 4: HB-SL Molecular Structure



PERFORMANCE

Refrigeration oil requires good chemical stability (especially in POE for hydrolytic stability), lubricity, material compatibility and other various characteristics. In order to meet these requirements, oils especially for HFC type applications, must have not only a better quality base oil, but also an effective additive formulation. Taking into consideration of the above required qualities, this paper presents the data on solubility with refrigerants, chemical stability and lubricity of HB-SL.

Solubility:

In the first place, the reason why POEs were used as a synthetic refrigeration oil for HFC refrigerant, was that mineral oils were not soluble with HFC. In other words, solubility with refrigerants was the first characteristic to clear for the refrigeration oil to be considered.

In Fig.1 and Fig.2, the solubility data of HB-SL for R407C and R410A is shown. The solubility of refrigeration oil in refrigerants is dependent on the characteristic of the base oil and may be not adjusted by additive formulation. In the case of HFC refrigerant and POE, the solubility depends of the molecular structure of alcohol and fatty acids. The lower side critical solution temperature (L-CST) of HS-POE (VG68) with R410A is poor at +10°C. In comparison to this, L-CST of HB-SL with R410A is better at -17°C. Therefore, HB-SL has the advantage in oil return from the low side of the refrigeration cycle and heat pump application in cold weather.

HB-SL is very soluble in R407C as shown.

Fig. 1: Mutual solubility of R410A

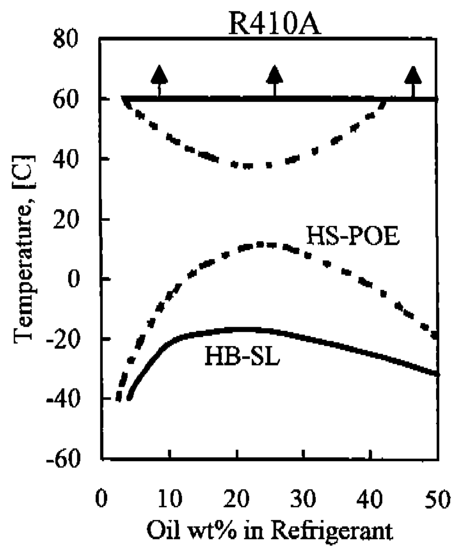
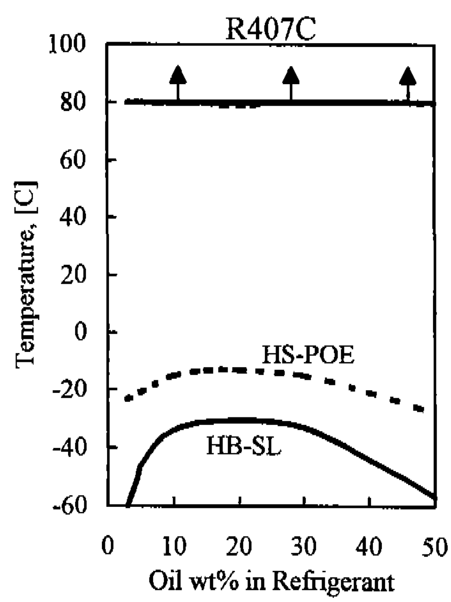


Fig. 2: Mutual solubility of R407C



Hydrolytical Stability:

Hydrolytic stability is a very important characteristic. Hydrolysis of POE results in fatty acids, which are harmful to the refrigeration system. Hydrolytical stability as measured by the sealed tube method is shown on Fig.3 to Fig.5. Having a partial alpha branched structure, it is easy for water to attack the ester group of HS-POE. As a result, the total acid number increases rapidly and in order to prevent this, HS-POE is dependent on the use of an epoxy type additive.

Fig. 3: Hydrolytical Stability-Effect of water

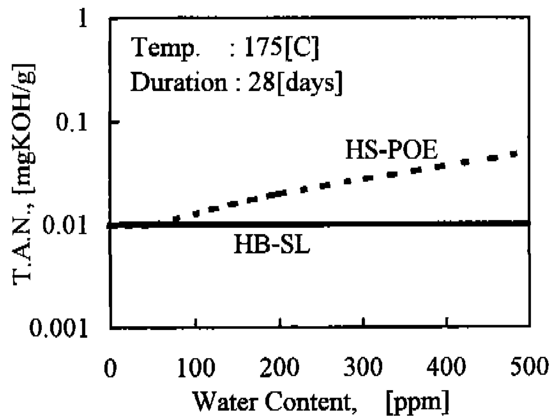
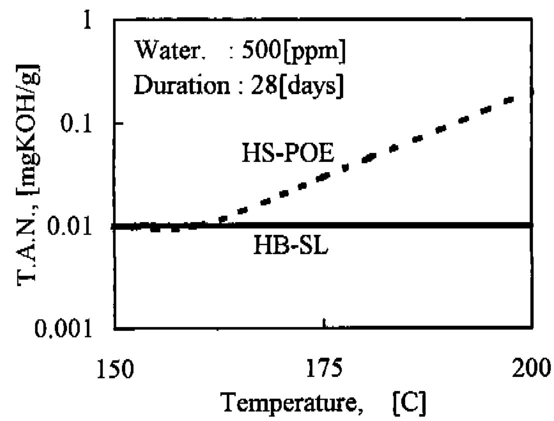
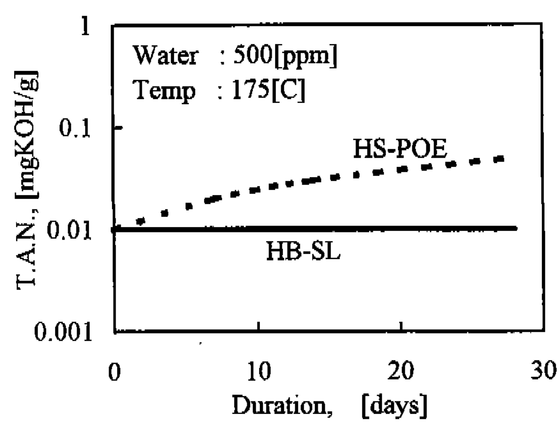


Fig. 4: Hydrolytic Stability-Effect of temperature



On the other hand, HB-SL has alpha carbon atom bonding with two alkyl groups which makes it a highly steric hindrance for ester group. As a result, the hydrolytic stability is excellent as compared to the HS-POE, the total acid number does not increase.

Fig. 5: Hydrolytic Stability-Effect of time



Lubricity:

To promote proper lubrication in the system, the chloride atom in the refrigerant is beneficial for adequate lubrication. Therefore, if a chloride free HFC refrigerant is used, a higher level of lubricity is required in the oil than in the past.

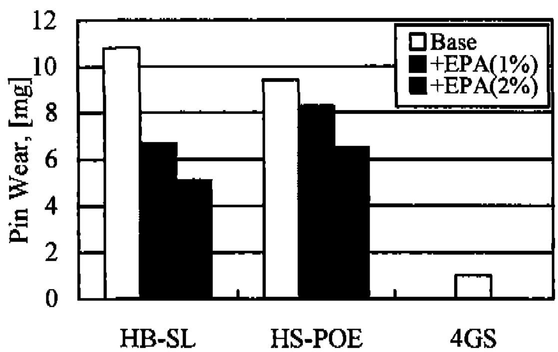
The Falex test is normally used to measure lubricity by failure load and pin wear as data results shown in Table 1. In general, synthetic refrigeration oils like POE for HFC refrigerants as compared to naphthenic oils, the failure load is high but pin wear rate is slightly poor. Especially, with the refrigerant, pin wear rate of the naphthenic oil 4GS(VG56) is lower than that of POE.

Table 1. Falex test results (Failure Load)

Failure Load, lbs	HB-SL	HS-POE	4GS(VG56)
Base Oil	1,000	1,000	530
+ EPA*(1%)	1,050	1,050	780
+ EPA*(2%)	1,100	1,050	900

*Extreme Pressure Additive

Fig.6 : Falex test results (Pin Wear Test)



At this point, we have conducted compressor endurance tests with two kinds of refrigerants(R407C and R410A) and analyzed the parameters. The test results are as shown in Table 2A and Table 2B.

Table 2A. Compressor Endurance Test Results-R410A/HB-SL

Compressor Type	RO	RO	RO	RO	RO	RO
Application	RAC	RAC	RAC	RAC	RAC	RAC
Modification of compressor	Yes	Yes	Yes	Yes	Yes	No
EPA	Yes	No	Yes	No	Yes	No
Test Condition	HSC	HSC	HSC	HSC	HLC	HLC
Duration, [hrs]	700	700	2000	4000	2000	2000
Wear	Pass	Pass	Pass	Pass	Pass	Pass
Copper Plating	No	No	No	No	No	No
Deterioration of oil	No	No	No	No	No	No
Decomposition of refrigerant	No	No	No	No	No	No

Table 2B. Compressor Endurance Test Results-R407C/HB-SL

Compressor Type	RO	RO	RO	RO	RO	RO
Application	RAC	RAC	RAC	RAC	RAC	RAC
Modification of compressor	No	No	No	No	No	No
EPA	Yes	No	Yes	No	No	Yes
Test Condition	HSL	HSL	HSL	HLC	HLC	HLC
Duration, [hrs]	1000	1000	2000	2000	2000	2000
Wear	Pass	Pass	Pass	Pass	Pass	Pass
Copper Plating	No	No	No	No	No	No
Deterioration of oil	No	No	No	No	No	No
Decomposition of refrigerant	No	No	No	No	No	No

Test Condition HSL : High Speed High Load Continuous
HSC : High Speed Continuous
HLC : High Load Continuous
Compressor Type RO : Rotary Compressor
Application RAC : Room Air Conditioner

The above tables show satisfactory results on lubricity and passing range levels for the wear and other items. Although not shown in figures, we have found that the test for HB-SL with extreme pressure additive shows significantly better results. Although the Falex pin wear test results of Fig. 6 do not reflect positive results, actual compressor endurance test runs are more reliable for data purposes. The tested oil analysis showed that the oil has not deteriorated and copper plating or sludge did not occur.

CONCLUSION

1. A 100% alpha branched structure HB-SL was developed by advanced and unique synthesis method.
2. HB-SL has significantly better solubility with R407C and R410A as compared to HS-POE.
3. HB-SL has the most advantage in hydrolytic stability.
4. The actual compressor endurance test is a more reliable test method which shows HB-SL passing the lubricity requirements as opposed to the Falex test method.
5. HB-SL production process, when compared to HS-POE production stages, is a cost savings process.

REFERENCES

(1)Technology of Mitsubishi Gas Chemical, Inc