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ABUSTRACT

Cost-reduced ester lubricants with brand new chemistries have been developed. In regard to their general properties such as miscibility and solubility with HFCs, hydrolytic stability, lubricity, and hygroscopicity, the new esters showed the same or better results compared with current POEs. Compatibility tests with organic materials and contaminant precipitation tests at low temperature were also conducted, and it was confirmed that the new esters have equal or better results as well. The new esters provided very promising results in compressor durability tests compared with the current popular POE.

INTRODUCTION

After the adoption of the Montreal Protocol in 1987, many types of lubricants have been developed as refrigeration lubes for HFCs, and four major chemistries, polyalkyleneglycol, polyolester, polyvinylether, and alkylbenzene, are currently used in various applications. In particular, polyolesters (POEs) have been widely used worldwide as lubes for household refrigerators with R134a, and they have begun to be applied to air conditioners as well. POEs are widely adopted because 1) POEs have good miscibility and solubility with HFCs ;2) POEs possess good insulation properties ; 3) POEs are globally available. [1] In Japan, branched POEs (B-POEs), which are made from polyols and branched acids, have been widely used in order to obtain higher stability and reliability. In Europe, linear acids are generally used in the chemistries, and it is said that linear POEs (L-POEs) show better lubricity. L-POEs can be produced more economically as well. Both B-POEs and L-POEs have been used for more six or seven years without any major problems. Immiscible alkylbenzene (AB) has been adopted for rotary refrigerators with R134a in Japan. At present, AB with low viscosity has expanded its market territory into vending machines with R407C, dehumidifiers with R134a, and even split air conditioners with R407C and R410A. [2] [3] Although AB is much less expensive than POEs and shows excellent reliability, it cannot be universally applied to the current systems because it is barely miscible with HFCs. Sometimes system modifications are needed to apply these unique lubes.

We have developed new chemistries to meet the following criteria:

1) Miscibility with HFCs.
2) Performance and properties that are equal to or better than those of the current POEs.
3) Stronger resistance to contaminants such as metalworking fluids.
4) Lower cost than with current POEs

In this paper, the features of the new esters, including their physical and chemical properties, lubricity, material compatibility, and the tendency of the contaminants to precipitate, are reported. Durability with reciprocating compressors is also described.

CHEMICAL STRUCTURE AND PHYSICAL PROPERTIES OF NEW ESTER LUBES

The current POEs for household refrigerators consist of di-, tri-, and tetra-functional hindered polyol such as NPG, TMP, and PE, and mono-functional organic acids with carbon numbers from 5 to 9. The new esters (NEs) are synthesized from di-functional organic acids and mono-functional alcohol. Two different types are available depending on the chemistry. Type A has unsaturated bonding in the molecule, and it can provide excellent cost performance. Type B is a saturated product, and it shows higher stability than the B-POEs. The general properties of the NEs that were used in this study are shown in Table 1. In this study, NEs with ISO VG10 and VG15 were used. B-POE VG10 and L-POE VG10 were also evaluated as references.

EXPERIMENT AND DISCUSSION

Miscibility with R134a

The phase separation curves with R134a are shown in the figure. Both Type A and Type B show better miscibility than L-POE. NEs with higher viscosity show higher critical solubility temperatures.

Hydrolytic Stability

Generally, esters are decomposed by hydrolytic reactions. In order to confirm the stability, typical hydrolytic stability tests (bomb tests) were conducted with 500-ppm moisture. The test conditions are shown in Table 2. After the tests, the TAN, the sludge formation, and the appearance of the lubes and catalysts were checked. The test results are shown in Table 3. The increase in TAN for the NEs is much smaller than that for the L-POE and almost equal to that for the B-POE. No sludge formation and no change in the appearance of the catalysts were observed. Even B-POE changes the appearance of the surface of the steel catalyst after the sealed tube or bomb tests due to the chemical reaction of the steel and the organic acids from the POEs. The NEs did not show any change in the appearance of the steel surface because the reactivity of the acid from the NEs is very low and the corrosivity to metals is also negative.

Lubrication Properties

a. FALEX Seizure Load Tests

FALEX seizure load tests were conducted following ASTM D3233-86. R134a was blown into the oil pan at a rate of 10 liters per hour. The tests were run at room temperature. The test results are shown in Table 4. For the POEs, the L-POE had a higher seizure load than B-POE, as is generally reported. For the NEs, Type A showed a higher seizure load than Type B. When the NEs and POEs were compared, the seizure load of Type A was equal to that of the L-POE and the seizure load of Type B was higher than that of the B-POE.

b. FALEX Wear Test

FALEX wear tests were also conducted. An aluminum alloy pin and a standard v-block were used as the specimens. The tests were conducted at 80 (+/- 2) degrees C while blowing R134a into the oil pan. After break-in running at 100 lbs for 5 minutes, the tests were conducted at 200 lbs for 1 hour. After the tests, the wear to the pin and v-block was measured by weight. The test results are shown in Table 5. These results show that the total wear amount for NEs is smaller than that for POEs.

Hygroscopicity

The hygroscopicity of NEs was measured. Samples with an initial moisture level of less than 10 ppm were prepared. Each sample of 5 grams in a beaker was placed into the testing box, which was held at a constant temperature of 25 degrees C and a constant humidity of 80% RH. The samples were left in the box for three days, and then the moisture level was measured. As shown in Table 7, the hygroscopicity of the NEs is confirmed to be similar to that of the POEs.

Compatibility with Organic Material

The compatibility of the NEs with PET film was evaluated. For the insulating film, low-oligomer PET film was used in the tests. Several pieces of dumbbell-shaped PET film were put in an autoclave with the sample lube, and the bomb was filled with R134a. Aging tests were done at 135 degrees C for 21 days. After the tests, the changes in weight, tensile strength, and extension were evaluated (Table 6). The effect of the NEs on the PET film seems to be equivalent to that of the B-POE.

Dissolution of Contaminants

One of the largest issues to be resolved when POEs were adopted for household refrigerators was sludge formation due to contaminants from processing fluids. As sludge causes capillary plugging, it is very important to control sludge formation. If sludge is soluble with the base stock, no capillary problems will occur. Therefore, it is necessary for the base stock to have better solubility with contaminants. In order to determine the solubility with contaminants, precipitation tests were conducted with various metalworking fluids such as rust preventing fluids, cutting fluids, and drawing fluids at low temperature. One portion of the test samples with 2000 ppm of rust preventing or cutting fluids and nine portions of R134a were placed into pressure-proof glass tubes and maintained in a cold bath at minus 20 degrees C. The precipitation status was observed then. Test samples with 1000 ppm or 5000-ppm polybutene (PB), the main component of copper drawing fluid, were also evaluated in the same way. The test results are shown in Tables 8 and 9. In the contaminant tests with rust preventing and cutting fluids, no precipitation was observed with either the B-POE or NEs. However, the test results with PB were different. PB was precipitated from the B-POE in five hours with the 1000-ppm sample and in one hour with the 5000-ppm sample, but no precipitation was found from the NE samples. The NEs were thus proved to have higher solubility with contaminants such as PB.

Compressor Durability Tests

Finally, compressor durability tests were conducted using small reciprocating compressors (displacement: 4 cc) for 1000 hours. The test conditions were Pd = 2.4 MPa, Ps = 0.1 MPa, and Td = 100 degrees C, and the tests were conducted with a short loop circuit. As a reference, the current compressor with L-POE (the current lube for the tested compressor) was tested. After the tests, the compressors were taken apart, and the mechanical parts and lubes were recovered and analyzed. No wear and no changes in the appearance were observed for the mechanical parts, and no damage caused by the lubes was observed. However, slight copper plating was found in the current compressor with L-POE.

CONCLUSIONS

New esters (NEs) were developed, and it was proved that they possess sufficient miscibility and solubility with HFCs as well as sufficient lubricity and thermal and chemical stability. NEs have extremely low metal corrosivity compared with the current POEs. As the NEs have the same level of hygroscopicity, no special handling is required. The NEs are stable with metalworking fluids. In particular, the NEs have better solubility with polybutene, which is the main contaminant from copper drawing fluids, than do POEs and they can prevent bad effects on capillaries. The NEs performed just as well as L-POE and showed as good compressor durability test results as those obtained with the current L-POE. The NEs can be used in place of conventional miscible POEs without any alterations to the compressors, and they can help to reduce costs.

REFERENCES

[1] T. Sakamoto , et al., The International Symposium on HCFC Alternative Refrigerants'98 (1998) 89.

[2] M.Saito, et al., The International Symposium on HCFC Alternative Refrigerants'96 (1996) 148.

[3] M.Sunami , et al., Int. Refrigeration Conf. , Purdue(1998) 355.

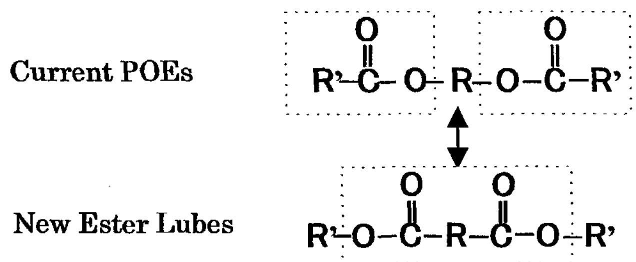

Figure 1. Structure of New Ester Lubes and Current POEs

Table 1. General Properties of NEs

			NE-A VG10	NE-A VG15	NE-B VG10	NE-B VG15	B-POE VG10	L-POE VG10
Density	@ 15 deg. C	g/cm^3	0.981	0.974	0.971	0.962	0.926	0.951
Flash point	COC	deg. C	198	200	198	200	200	220
K. viscosity	@ 40 deg. C	mm^2/s	12.1	15.4	12.7	15.7	10.6	9.9
	@ 100 deg. C	mm^2/s	2.6	3.1	2.7	3.2	2.6	2.8
VI			9	26	7	25	56	124
T.A.N.		mgKOH/g	0.01	0.01	0.01	0.01	0.01	0.01
Color		ASTM	L0.5	L0.5	L0.5	L0.5	L0.5	L0.5
Pour point		deg. C	LT-45	LT-45	LT-45	LT-45	LT-45	LT-45
Dielectric breakdown		kV	60	60	60	60	60	60
Resistivity	r.t.	Ω·cm	$5*10^{12}$	$5*10^{12}$	$3*10^{13}$	$3*10^{13}$	$5*10^{13}$	$4*10^{12}$
Stability	175 deg. C	ASTM	L0.5	L0.5	L0.5	L0.5	L0.5	L0.5
with R134a	*14 days	Sludge	None	None	None	None	None	None

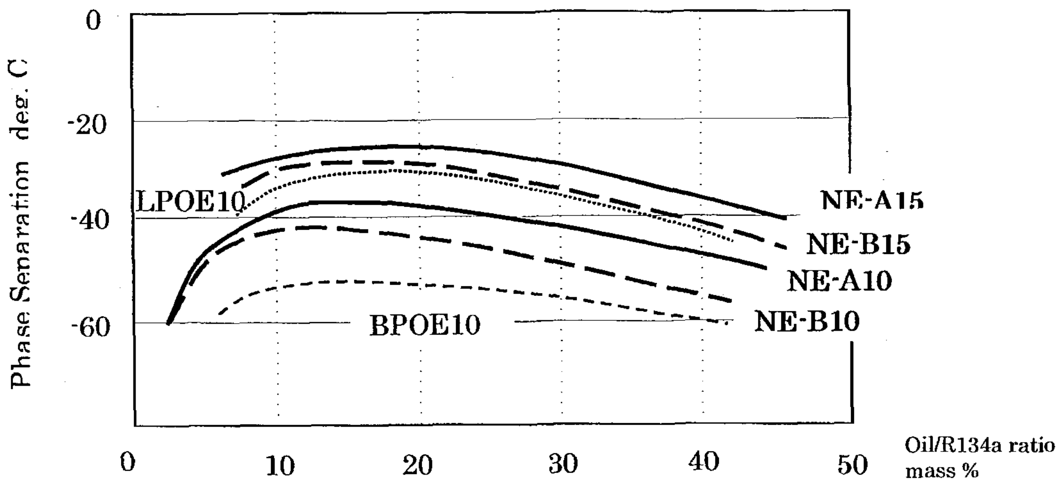

Figure 2. Phase Separation Temperature with R134a

Table 2. Test Conditions for Hydrolytic Stability Test (Bomb Test)

Refrigerant	R134a
Temperature	175 degrees C
Test period	14 days
Moisture	500 ppm
Catalysts	Steel, copper, aluminum wire

Table 3. Hydrolytic Stability Test Results

	NE-A VG10	NE-A VG15	NE-B VG10	NE-B VG15	B-POE VG10	L-POE VG10
Color ASTM	L0.5	L0.5	L0.5	L0.5	L0.5	L0.5
Change in steel	None	None	None	None	Loss of luster	Loss of luster
Change in copper	None	None	None	None	None	None
Sludge	None	None	None	None	None	None
TAN mgKOH/g	0.06	0.05	0.05	0.05	0.05	1.7

Table 4. FALEX Seizure Test Results

	NE-A VG10	NE-A VG15	NE-B VG10	NE-B VG15	B-POE VG10	L-POE VG10
FALEX seizure load, lb (ASTM specimen)	1250	1250	1200	1200	1100	1250

Table 5. FALEX Wear Test Results (Steel/Aluminum)

	NE-A VG10	NE-B VG10	B-POE VG10	L-POE VG10
Wear loss to pin (aluminum) mg	1.4	0.2	0.3	0.2
Wear loss to v-block (steel) mg	4.3	6.3	10.1	9.2

Table 6. Compatibility with PET film

	NE-A VG10	NE-A VG15	B-POE VG10
Change in weight %	+1.4	+1.3	+1.1
Change in tensile strength %	-5.1	-5.3	-5.0
Change in extension %	-19.2	-18.4	-21.6

Table 7. Hygroscopicity (Saturated Moisture Level) ppm

	NE-A VG10	NE-A VG15	NE-B VG10	B-POE VG10	L-POE VG10
25 degrees C, 80% RH ppm	1690	1520	1590	1380	1800

Table 8. Precipitation of Contaminants

	NE-A VG10			B-POE VG10		
	Rust Prv*1 2000 ppm	S-CTG*2 2000 ppm	Cl-CTG*3 2000 ppm	Rust Prv*1 2000 ppm	S-CTG*2 2000 ppm	Cl-CTG*3 2000 ppm
1 hour	Clear	Clear	Clear	Clear	Clear	Clear
3 hours	Clear	Clear	Clear	Clear	Clear	Clear
5 hours	Clear	Clear	Clear	Clear	Clear	Clear

Rust Prv*1: Rust preventing fluid

S-CTG*2: Sulfur type cutting fluid

Cl-CTG*3: Chlorine type cutting fluid

Table 9. Precipitation of Polybutene (10,000 mm^2/s)

	NE-A VG10		B-POE VG10	
Dosage	1000 ppm	5000 ppm	1000 ppm	5000 ppm
1 hour	None	None	None	Precipitated
3 hours	None	None	None	Precipitated
5 hours	None	None	Precipitated	Precipitated

Table 10. Compressor Durability Test Results with NEs and POE

	NE-A VG10	NE-A VG15	L-POE VG18
Piston	O.K.	O.K.	Copper plating
Piston pin	O.K.	O.K.	O.K.
Con-rod	O.K.	O.K.	O.K.
Shaft	O.K.	O.K.	O.K.
Discharge valve	O.K.	O.K.	Color change
Recovered oil	No change	No change	No change

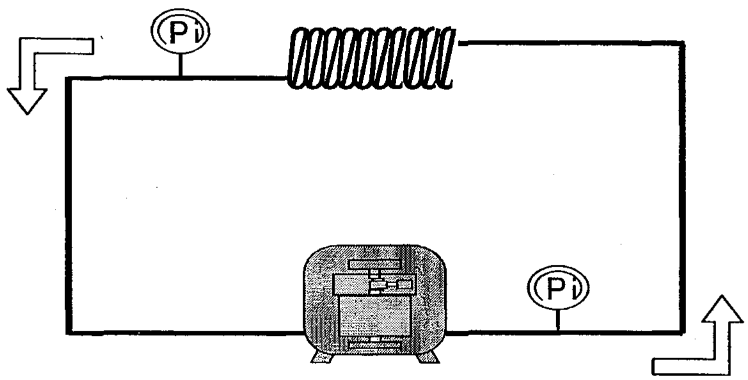

Figure 3. Schematic Diagram of Compressor Durability Test