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NEW LUBE OIL FOR STATIONARY AIR CONDITIONER

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ABSTRACT

Replacing R-22 by HFC refrigerants in stationary air conditioners is forcing oil producers to develop a new lubricant which has good miscibility with HFC, lubricity and electric resistivity.

Mitsui has selected a carbonate compound for a new lubricant candidate with HFC and developed it forcusing on its thermal stability, which is one of the most important factors to get good lubricity.

By suppressing the hydrogen bond between ß-position H and a carbonate group, Mitsui has successfully synthesized the new carbonate type lubricant.

This new carbonate type lubricant has good thermal stability, lubricity which is almost the same level as SUNISO 4GS, miscibility with SUVA AC-9000 and high electric resistivity and forms no acids by its decomposition.

INTRODUCTION

R-22 refrigerant which is used in stationary air conditioners is to be abolished completely by the year 2020. Replacement HFC refrigerants are not compatible with mineral oils and a new lubricant is required. This new lubricant must have a viscosity grade of about VG68, good miscibility with the new refrigerant, high electric resistivity, thermal stability and lubricity.

Ester, ether and carbonate compounds have been evaluated. Ester type products have corrosion problems due to their tendency to form acids while ether type products demonstrate poor miscibility and electric resistivity.

Carbonate types have good miscibility, electric resistivity and corrosion properties (don't form acids), but poor thermal stability and lubricity[1) 2)].

This paper introduces a new carbonate oil for stationary air conditioners which shows singnificant improvements in thermal stability and lubricity.

EXPERIMENTALS

1. Synthesis of Carbonate

Various carbonates were synthesized by reacting dimetyl carbonate with alcohols under catalyst (eq. 1).

$$CH_3OCO_2CH_3 + 2ROH \rightleftharpoons ROCO_2R + 2CH_3OH \qquad \text{(eq. 1)}$$

If necessary, carbonates obtained were modified.

2. Miscibility for Refrigerant

Critical solubility was measured based on JIS K-2211.

3. Thermal Stability

Evalution of thermal stability was carried out by means of sealed tube test.

Test Condition Oil / Refrigerant = 1 / 1 (wt. ratio)
Fe, Cu, Al wires added
Temp. : 150, 175, 200 °C,
Time : 28 days

Carbonates produce a small amount of CO_2 when they were thermally decomposed. Therefore, thermal stability of carbonates was evaluated by CO_2 content in the whole gases.

4. Lubricity

Lubricity was measured by using Friction Testing Machine under high pressure and Falex Machine.

RESULTS AND DISCUSSION

1. General Properties of Carbonate

1.1 Miscibility and Electric Resistivity

Table 1 shows that the dipole moment of the ternary refrigerant is higher than R-22. This means that the new refrigerator oil also needs a high polarity if it is to be miscible with the replacement HFC refrigerants. Table 1 also shows the polarity of a comparably simple ester, ether and carbonate. As you can see, the carbonate has a high dipole moment and is more polar. Thus it is possible to conclude that the carbonate moiety is an effective way to insure miscibility.

Table 1 Dipole Moment of Freons and Chemicals *1)

Freon 3)		Chemicals Containing Oxygen Atom 4)		
R - 22 $CHClF_2$	Ternary Refrigerant (SUVA AC-9000)	Dimethyl ether CH_3-O-CH_3	Methyl Acetate $CH_3-C(=O)-O-CH_3$	Dimethyl Carbonate $CH_3-O-C(=O)-O-CH_3$
1.46	1.92 *2)	1.25	1.82	3.32

*1) Unit : Debye
Calculation : MNDO-PM3 MO Method
*2) Weighted mean value of R-134a, R-32 and R-125

In general, an oxygen atom increases polarity of a base oil. However electric resistivity decreases with an increasing presence of oxygen.

Data suggests that carbonates are more forgiving with respect to this rule than either esters or ethers (Fig. 1).

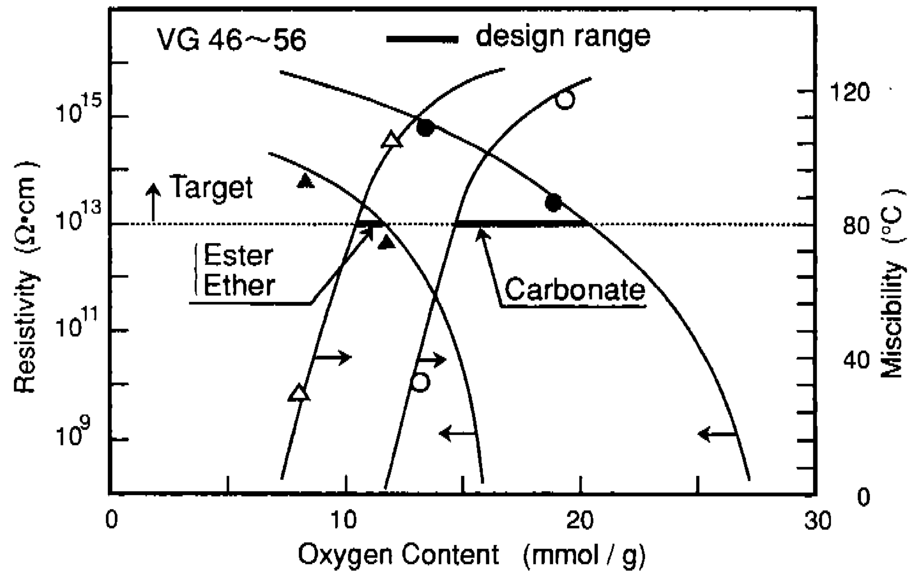


Fig.1 Relationship between Miscibility, Resistivity and Oxygen Content

1.2 Lubricity

The main factors which control oil's lubricity are metal wetting and thermal stability of oils (eq. 2).

$$\text{Lubricity} \fallingdotseq \text{Wetting} \times \text{Thermal Stability} \qquad \text{(eq. 2)}$$

Good metal wetting means strong chemical interaction (affinity) between an oil and metal. Based on this consideration, the affinity between ester, ether, carbonate and iron was examined using IR method. The results showed that a carbonate possessed the strongest affinity among them (Table 2).

Stronger affinity of a carbonate is due to higher electron density on the oxygen atom (Table 3).

From IR results, carbonates are considered to have potentially good lubricity.

Table 2 Relationship between Affinity and Chemical Structure

Candidate Chemicals		Absorbance Ratio*1)	
		C = O	COC
Ester	Lubricant only	4.1	—
	Lublicant on steel	4.1	—
Ether	Lubricant only	—	2.9
	Lublicant on steel	—	2.9
Carbonate	Lubricant only	4.3	—
	Lublicant on steel	2.1	—

*1) Stronger Affinity is bigger deviation from Absorbance Ratio of Lubricant only.

Table 3 Electron Density on Oxygen Atom

Compound	Electron Density*1) (Relative Value)
Dimethyl Carbonate	– 1.00
Methyl Acetate	– 0.88
Dimethyl Ether	– 0.85

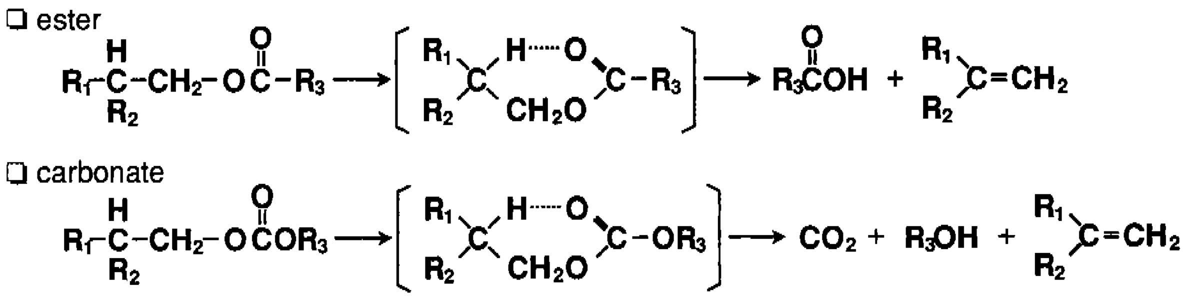
*1) Culculation : CNDO2

We selected a carbonate compound for a new lubricant candidate with HFC refrigerants and made researches into thermal stability and lubricity which were insufticient in previous carbonates.

2. Improvement of Thermal Stability

Thermal stability is one of the most important factors to get good lubricity, therefore our studies were focused on the improvement of thermal stability.

Thermal decomposition of carbonate occured in a similar scheme to that of ester. [5]



The formation of hydrogen bond between ß-position hydrogen and a carbonate group was a key step for decomposition. Therefore we designed molecular structures with the goal of suppressing the hydrogen bond formation and found a new remarkably improved carbonate.

CO_2 value of the new carbonate was reduced to about 1/50 the level of previous carbonates (Table 4).

The influence of water content on CO_2 generation was also examined. As the result of it, no influence of water content was observed on the amount of CO_2 generation in the range of 100~1000ppm. Total Acid Number(TAN) wasn't increased at all, while TAN increase and sludge formation were observed in the case of ester (Table 5).

These results suggest severe control of water is necessary to suppress acid and sludge formation when ester oils are used, whereas this control is not required in the case of carbonate oils.

TAN of ester was more than that expected from the mole number of water contained. This means that acid from ester was produced by not only hydrolysis but also thermolysis.

Table 4 CO_2 Generation of New Carbonate *1)

Temp. (°C)	CO_2 (vol·%)		
	Former Carbo.	New Carbo.	Ester
150	0.08	0.03	0.01
175	0.68	0.06	0.02
200	5.08	0.10	0.02

*1) 28 days
Water : 100 ppm

Table 5 Effect of water on CO_2 Generation *1)

Water (ppm)	CO_2 (vol·%)		
	Former Carbo.	New Carbo.	Ester
100	0.68 (0.01)	0.06 (0.01)	0.02 (1.35)
500	0.75 (0.01)	0.08 (0.01)	0.02 (2.30)
1000	0.77 (0.01)	0.08 (0.01)	0.02 (3.50)

*1) Temp. : 175°C / 28 days
( ) : TAN mgKOH/g

3. Lubricity

As mentioned above, we successfully synthesized the new carbonate compound which has good thermal stability, that is, this new carbonate is expected to have good lubricity.

Lubricity of the new carbonate was evaluated by measuring wear using the Testing Machine shown in Fig.2. Test results are summarized in Table 6. The new carbonate showed an improvement of lubricity as we expected and wear amount at high temperature was reduced to almost the same level as SUNISO 4GS.

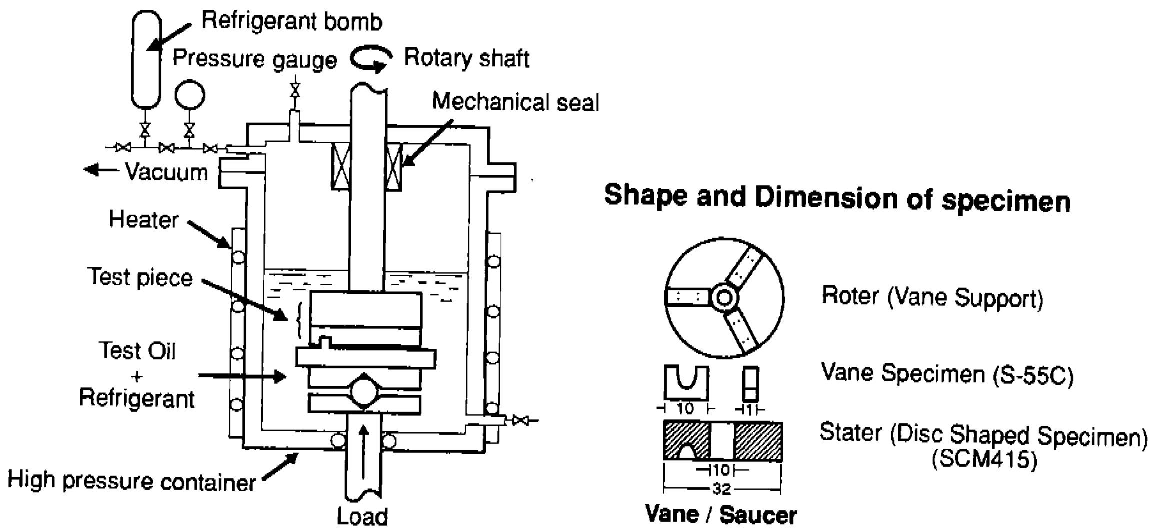


Fig. 2 Friction Testing Machine under High Pressure

Table 6 Lubricity   Test Condition : 80°C, 125°C, 200kg/cm2, 500rpm. Oil/Refrigerant=80/20 (wt./wt.)

Oil		New Carbo.		Former Carbo.		Ester		SUNISO 4GS	
Temp.(°C)		125	80	125	80	125	80	125	80
Wear (mg)	Vane	50.0	44.2	124.4	92.8	93.4	67.0	52.3	16.8
	Disk	0.8	0.2	2.3	1.2	2.9	4.2	0.6	0.6
	Total	50.8	44.4	126.7	94.0	96.3	71.2	52.9	17.4
TAN (mgKOH / g)		0.01	0.01	0.01	0.01	0.08	0.08	0.01	0.01
Refrigerant		R134a		R134a		R134a		R22	

4. Typical Properties of New Carbonate

Basic properties are shown in Table 7. Fig.3 shows the critical solubility curve with the ternary refrigerant and Fig.4 presents water absorption curve.

These properties show that the new carbonate oil has good miscibility, electric resistivity and lubricity. Water absorption is approximately equal to that of a ester oil.

Table 7 Typical properties of New Carbonate

Properties		Former Carbo.	New Carbo.	Ester
Viscosity	cSt/40°C	56	63	61
Miscibility*1) Lower/Higher °C		−40/80<	−35/80<	−30.80<
Resistivity	Ω•cm	$2x10^{14}$	$4x10^{13}$	$1x10^{13}$
TAN	mgKOH/g	0.01	0.01	0.01
Falex (wear)*2)	mg	10.0	2.3	12.5

*1) Miscibility : SUVA AC-9000 (HFC-134a/HFC-125/HFC-32)
*2) Falex : Mineral Oil 1.0mg

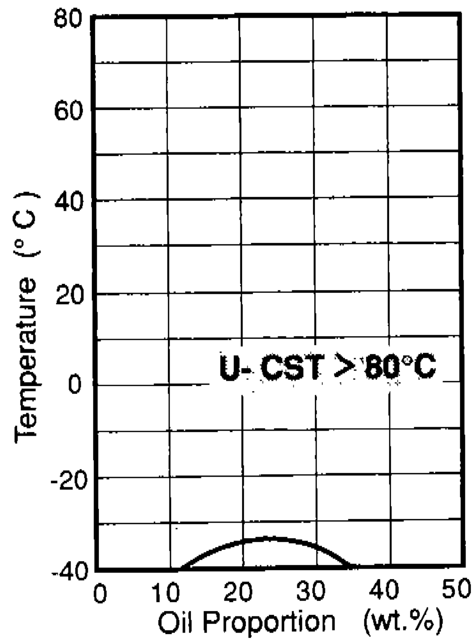


Fig.3 Critical Miscibility Curve of New Carbonate with SUVA AC- 9000

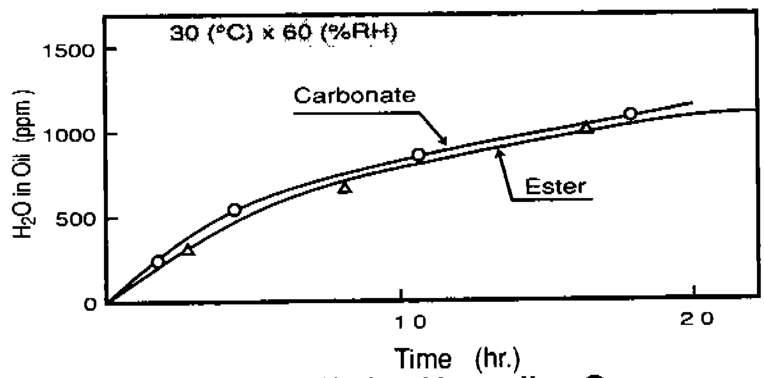


Fig.4 Water Absorption Curve

CONCLUTION

(1) Based on studies of model chemicals, it is suggested that carbonate has superior miscibility and lubricity to ester and ether.
(2) Carbonate shows less hydrolysis than ester and doesn't increase acid value.
(3) By improvement of molecular structures, a new carbonate which showed high thermal stability was developed.
(4) New carbonate provided good miscibility with the ternary refrigerant, electric resistivity and lubricity which was almost the same level as that of a existing mineral oil.

From the data above, it can be concluded that the new carbonate will become an excellent base oil for stationary air conditioner with R-22 alternative.

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