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CARBONATE OILS FOR UNITARY AIR CONDITIONERS WITH R-410A

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ABSTRACT

The authors have successfully developed new CARBONATE type lube oil for unitary air conditioners with R-410A.

Carbonate oils (VG32～68) have excellent R-410A (-36～60℃) miscibility and have good lubricity in 4 ball and FALEX tests under R-410A.

Carbonate oils also have good chemical and thermal stability .

Drop-in compressor test with carbonate oil had been carried out for 8000 hours demonstrating good lubricity and stability.

INTRODUCTION

R-22 refrigerant is to be abolished completely by the end of 2020. Consequently many kinds of alternative refrigerant for R-22 have been evaluated by compressor manufacturers.

R-407C was the first candidate, however, recently many compressor manufacturers have focused on R-410A and instead of R-407C because of its efficiency and better handling characteristics. As a consequence compressor manufacturers have been seeking suitable oils for R-410A.

The authors have successfully developed carbonate oils (VG32～68) with excellent R-410A miscibility which meet compressor manufacturers' demands.

RESULTS AND DISCUSSION

1. GENERAL CHEMICAL STRUCTURE OF CARBONATE OILS AND ROLES OF FUNCTIONAL GROUPS IN THE MOLECULE

General chemical structure of carbonate oils and roles of functional groups in the molecule are shown in Fig.1.

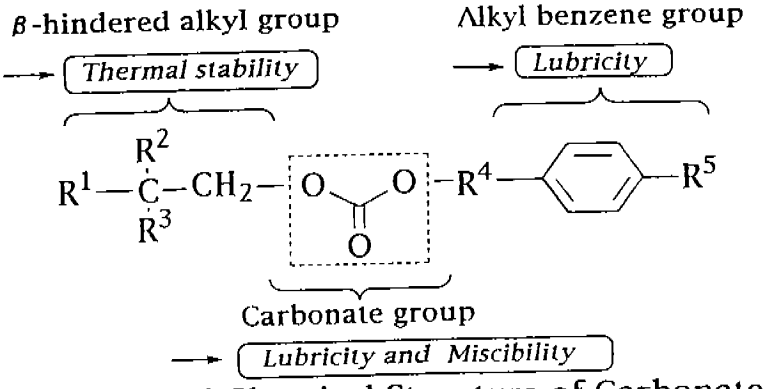

Fig.1 General Chemical Structure of Carbonate Oils

2. MISCIBILITY WITH R-410A

Carbonate group strongly polarizes the molecule yielding a higher dipolmoment. Consequently carbonate oils have good miscibility with R-410A which has a higher dipolmoment than R-22. (See Table 1 and Fig.2)

All viscosity grades of the author's carbonate oil have sufficient miscibility with R-410A as shown in Fig.2

Table 1 Dipolemoment of Freons and Model Compounds Containing Oxygen Atoms *1)

Freon		Model Compounds		
R-22 $CHClF_2$	R-410A *2) CH_2F_2 50% CHF_2CF_3 50%	Ether CH_3-O-CH_3	Ester O ‖ CH_3-C-O-CH_3	Carbonate O ‖ CH_3-O-C-O-CH_3
1.46	1.77	1.25	1.82	3.32

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

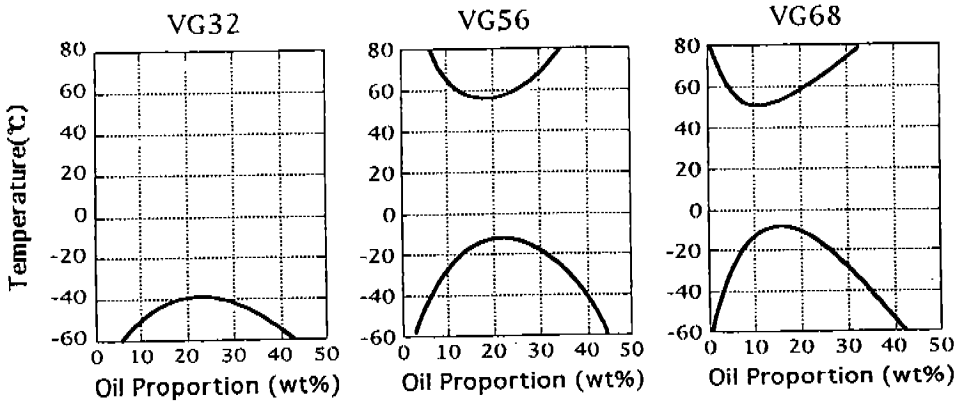

Fig.2 Critical Miscibility Curve of Carbonates with R-410A

3. THERMAL STABILITY

Thermal decomposition of carbonate compounds to CO_2 proceeds through a 6 membered ring intermediate which is formed by hydrogen bond formation between the β -position hydrogen and the carbonate group. (See Fig 3)

The authors have succesfully developed carbonate oils by designing a hindered alkyl group in which no β -position hydrogen exists in their molecule to give good thermal stability.

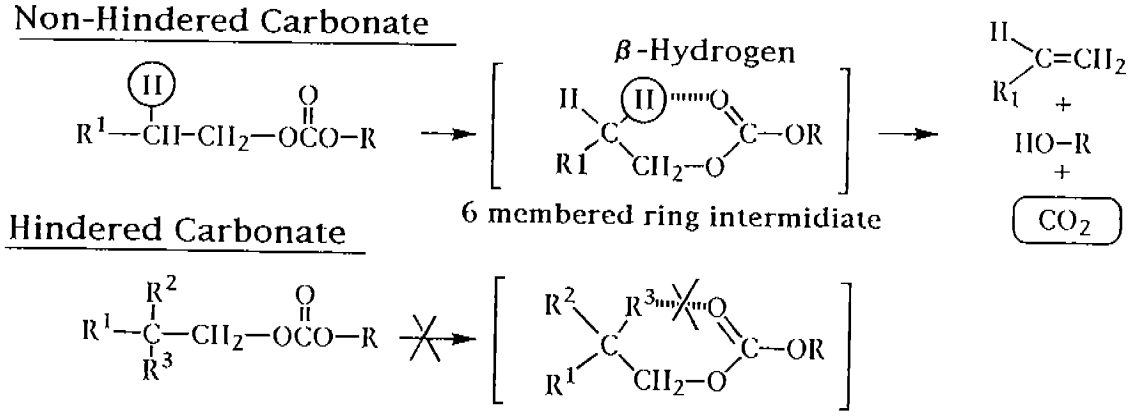

Fig.3 Thermal Decomposition of Carbonate

The temperature of thermal decomposition and the amounts of CO_2 evolved by thermal decomposition were measured by DSC and sealed tube tests respectively. Results are shown in Fig.4 , Table 2, and Table 3.

Fig.4 DSC Analysis Chart

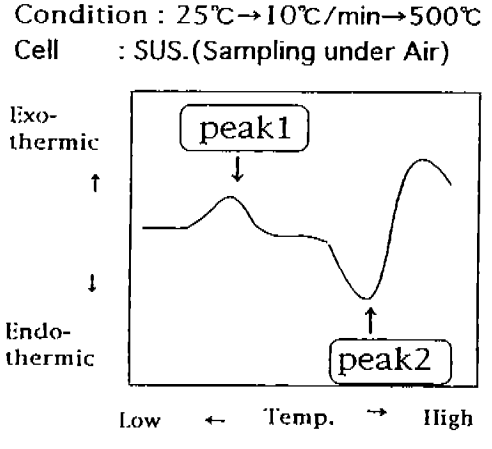

Table 2 Temperature of Decomposition of Carbonates

Oil	Temp. of Oxidation (peak1)	Temp. of Thermal Decmp. (peak2)
SA-4232 (VG32)	250.9	416.3
SA-4356 (VG56)	247.7	408.7
SA-4568 (VG68)	233.3	414.1
POE (VG68)	217.6	443.1
SUNISO 4GS (VG68)	194.7	489.3

Table 3 CO_2 Evolution of SA-4232/Sealed Tube Test

	Water [ppm]	Temp. [°C]	CO_2 (vol%)		
			7days	14	28
SA-4232	20	175	0.02	0.03	0.05
	500	175	0.04	0.07	0.07
POE	500	175	0.02	0.02	0.02

The temperature of thermal decomposition of carbonates are almost same as those of POE oil and Mineral Oil. On the other hand, temperature of oxidation of carbonate is highest among the oils tested.

The amounts of CO_2 evolved from carbonate (VG32) in sealed tube tests are less than 1000ppm under all tested conditions.

4. LUBRICITY UNDER R-410A

The main factors which control lubricity of oils are metal wetting (affinity), that is, the formation of a thin film of oil on the surface of a metal and its thermal stability.

Lubricity ≒ Wetting × Thermal Stability

The carbonate group has high electron density on its oxygen atom, therefore it is expected that carbonate group will have a strong affinity with the surface of metals (Table 4).

The lubricity of carbonate oils was examined by FALEX and 4ball tests under R-410A. Results are shown in Table 5.

The lubricity of carbonate oils under R-410A is better than POE and almost the same as that of Allkyl benzene under R-22 .

Table 4 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

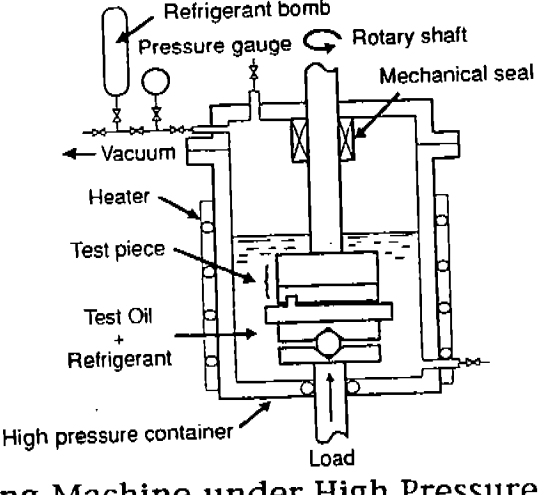

Fig.5 Friction Testing Machine under High Pressure

Table 5 Lubricity of SA-4232/High Pressure Friction and FALEX Test under R-410A

H.P.F. Test Condition

Specimen	4 balls (SUS-2)
Load × Time	981[N] (stepped up by 245[N/5min]) × 2[hours]
Rotation	500rpm
Oil amount	13ml
Oil Temp.	Initial ca.25 ~ 30 ℃ → Last ca.55 ~ 85 ℃
Refrigerant	Saturated Amount as Gas in Test Chamber

FALEX Test Condition

Load × Time	200[lbf] × 2[hours]
Rotation	290rpm

Oil	Refrigerant	H.P.F.Test	FALEX Test
		Wear (mm^2)	Wear (mg)
SA-4232(VG32) + EPA	R-410A	0.30	23.0
POE (VG32) + EPA	R-410A	0.85	26.5
Alkyl Benzene(VG32) + EPA	R-22	0.42	30.5

5. DROP-IN TEST WITH CARBONATE OIL (VG 68)

Drop-in test with carbonate oil (VG 68) in a rotary compressor was carried out for 8000 hours. Results are shown in Table 6.

Table 6 Drop-in Test With Carbonate

Test condition

Compressor : Rotary type 650[W] (With Inverter System)
Refrigerant : R-407C
Time : 8000hr

	Hindered Carb. +EPA(VG68)
Color ASTM	L2.0
TAN (mgKOH/g)	0.01
Sludge	No
CO2 (Vol%)	0.028
Wear Roller/Vane	○ / ○

Lubricity was excellent and the amount of CO_2 evolved by decomposition was less than 300ppm.

The temperature in a compressor with carbonate oil(VG68) was calculated to be about 160 ℃ by Arrhenius equation on the assumption that all amount of CO_2 is evolved by thermal decomposition.

Arrhenius equation ; $k = A\exp(-\Delta E/RT)$

$\Delta E = 29.3$kcal/mol, $A = 3.4 \times 10^{9}$, $k = 4.5 \times 10^{9}$ /day

(ΔE, k and A were measured (and calculated) by sealed tube tests without refrigerant and catalysts.)

6. TYPICAL PROPERTIES OF CARBONATE OILS

Table 7 Typical properties of New Carbonates

	SA-4232	SA-4356	SA-4568
Viscosity (cSt/40 ℃)	34.5	54.4	68.2
(cSt/100 ℃)	4.3	5.2	6.2
Viscosity Index	<0	<0	<0
Pour Point (℃)	-27.5	-35	-35
TAN (mgKOH/g)	0.01	0.01	0.01
Electric Resistivity (Ω·cm)	1.2×10^{13}	2.2×10^{13}	1.2×10^{13}

CONCLUSION

(1 The authors have successfully developed carbonate oils (VG32 ~ 68) with good R-410A miscibility.

(2) Thermal stability of carbonate oils are almost the same as that of POE.

(3) Lubricity under R-410A in FALEX and 4 ball tests is better than that of POE and almost the same as Alkyl benzene under R-22.

(4) Drop-in test with carbonate oil (VG68) / R-407C for 8000 hours demonstrates excellent lubricity and negligible CO_2 evolution.

(5) Carbonate oils (VG32 ~ 68) are on the TSCA inventry.