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ABSTRACT

In order to find proper lubricants for HFC-134a compressor system, many polar compounds have been synthesized and evaluated. Among such compounds, polyalkylene glycol (PAG) derivatives and carboxylates (esters) have been identified as candidates for car air-conditioners and for refrigerators respectively.[1)-3)] However, it is clear that these candidates have weaknesses:

PAGs - demonstrate poor miscibility of high viscosity types and high water absorption.

Esters - cause corrosion due to the generation of carboxylic acid upon degradation.

Our research has resulted in a new chemistry based on carbonates which overcome the shortcomings of the current candidate lube oils for both refrigerator and car air-conditioner compressors.

INTRODUCTION

The industrialized countries of the world have agreed to phase out production of chloroflourocarbon (CFC) which are depleting the Earth's ozone layer, by the year 2000. Due to the worsening conditions recorded this past year, President Bush recently decided to accelerate the ban by eliminating production in, and importation into the United States by December 31,1995. Among the possible CFC replacements, HFC-134a (hydrofluorocarbons) is the most likely candidate for replacing CFC-12 in car air conditioners and a good candidate for refrigerators. Conventional lubricants, mineral oils, which have been traditionally used in these applications with CFC-12, are not compatible with HFC-134a. In order to find an appropriate lubricant for HFC-134a compressor systems, many polar compounds have been synthesized and evaluated such as polyalkylene glycols (PAG's) derivatives and carboxylates (esters). However, both PAG's and esters have some shortcomings. Specifically, esters cause corrosion problems due to their tendency to degrade to calboxylic acids and PAG's are not miscible enough with HFC-134a at high temperatures.

In designing a new molecular structure for refrigerator and car air conditioner oil services, carbonates were considered because they have high polarity and do not degrade to acids. In introducing carbonates groups into molecules, we utilized dimethyl carbonate (DMC) [4)] and alcohols as raw materials. Typical properties and characteristics of the products based on this new carbonate chemistry are described below.

MOLECULAR STRUCTURE AND DIPOLE MOMENT

Comparing the dipole moments of the carbonate, ester, ether, HFC-134a and CFC-12, table 1 shows that the dipole moments of HFC-134a is higher than CFC-12. This means that the new base oils are to have high dipole moments to be miscible with HFC-134a. In order to increase the dipole moments of a base oil, it is necessary to bring polar groups into the molecular structure. Since the polarity of carbonate group is large in comparison to the ester group and ether group (table 1), the introduction of carbonate group into the molecule is very effective way to obtain excellent miscibility with HFC-134a. Although it is possible to introduce other hetero atoms into the molecule, only oxygen was selected to avoid problematic complications of side-reactions.

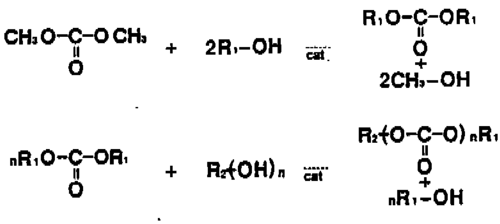
Table 1 Dipole Moment of Freons and Chemicals

Freon		Chemicals Containing Oxygen Atom		
R-12	R-134a	Dimethyl ether	Methyl Acetate	Dimethyl Carbonate
CF_2Cl_2	CFH_2CF_3	CH_3-O-CH_3	$CH_3-C(=O)-O-CH_3$	$CH_3-O-C(=O)-O-CH_3$
0.796	2.200	1.255	1.825	3.326

Unit : Debye
Calculation : MNDO-PM3 Molecular Orbital Method

SYNTHETIC REACTION

These carbonate based chemicals are synthesized by reacting DMC and various alcohols. It is noted that DMC is non-toxic as it is made from methanol and carbon monooxide while phosgene is very toxic. Another benefit of using DMC is that there is no trace chlorine contaminents in these products. Figure 1 shows the molecular structure where R_1,R_2 and n can be varied to generate target properties such as lubricity, viscosity, viscosity index, miscibility, electric resistance and thermal and chemical stability.



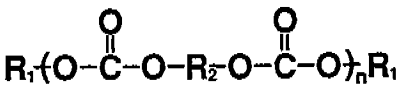
R_1 : C=2~10
R_2 : C=2~10
n : 1~2

Fig. 1 Synthetic Reaction

CARBONATES FOR REFRIGERATOR APPLICATIONS

Design Philosophy

A successful lubricant for use in refrigerator compressors using HFC-134a requires lubricity, high electric resistance, non-corrosiveness, miscibility over a broad temperature range with HFC-134a and chemical and thermal stability. Figures 2 and 3 show the molecular design and the molecular model. The intention was to minimize the density of the carbonate groups, make the molecule as linear as possible by attaching long alkyl groups and also minimize n. An extra benefit of this structure is that it is biodegradable.



R_1 : C=2~10 ; Lubricity and hydrophilic Control
R_2 : C=2~10 : Viscosity Index Control
n : 1~2 ; Viscosity Control
Density of Carbonate Group : Miscibility Control

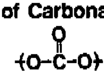
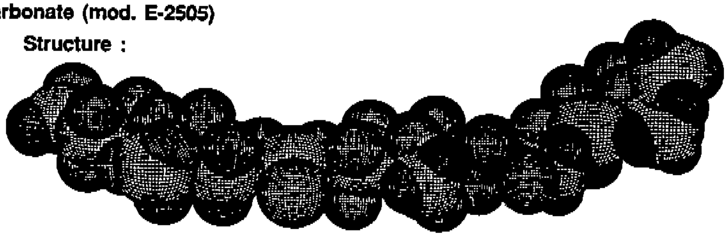


Fig. 2 Design Philosophy
(For Refrigerator Application)

Carbonate (mod. E-2505)

Structure :

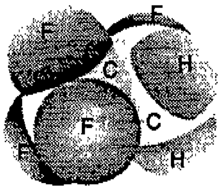


Dipole Moment : 2.158

Solubility Parameter : 9.06

Substitute Freon (HFC-134a)

Structure :



Dipole Moment : 2.136

Solubility Parameter : 7.95

Fig. 3 Molecular Structure & Dipole Moment

Typical Properties

High electric resistance requires a low density of polar groups while a wide range of miscibility with HFC-134a requires a high density of polar groups. These opposing requirements were satisfied by introducing highly polar carbonate groups into the molecules and controllings of its density. The basic properties of carbonate oils for refrigerator applications (table 2) and the critical solubility curve (figure 4) verify superoior electrical resistance and HFC-134a miscibility.

As the water absorption curve (figure 5) shows, our new base oil provides less hydrophilic property.

Table 2 Typical Properties of Oils for Refrigerators
(Comparison between Carbonates, Esters and Mineral oils)

Physical properties			Oils				
			Carbonate			Ester	Mineral oil
			mod.E-2508	mod.E-2505	mod.E-2504	Hindered polyole type	Suniso 4GS
Viscosity	100°C	cSt	7.4	6.0	3.8	4.2	5.8
	40°C		52	32.0	16.4	20	55
Viscosity index			104	136	125	107	-5
Pour point		°C	-45	-60.0	-55	-65	-45.0
Missibility in R-134a	High-temp.zone	°C	89	91	>100	>100	Insoluble
	Low-temp.zone		-65	-60	-51	-32	Insoluble
Falex value		1bf	820	880	780	1050	600
Resistivity		Ω·cm	1.8×10^{14}	3.3×10^{15}	6.0×10^{14}	2.0×10^{13}	5.0×10^{14}
Watter absorbancy			Middle	Middle	Middle	Middle	Low

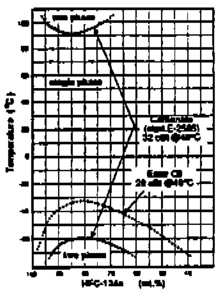


Fig 4 Critical Miscibility Curves of Oil with HFC-134a

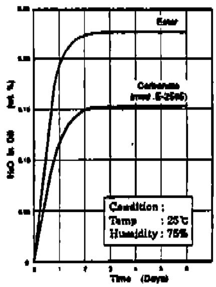


Fig. 5 Water Absorption Curve of Oils

Resistance to Heat, Water and Air

Tests were conducted to compare the thermal satability of carbonates and esters in the presence of water and air. These test were conducted by placing a sample consisting of 60 grams of base oil and 60 grams of HFC-134a with added water and air in an autoclave at 175°C for two weeks. The results as shown in table 3 demonstrate superior stability. Based on this table, the following comments can be made:

(1) There were no signs of corrosion on the metal test strip for the carbonate oil.
(2) The acid value did not increase for the carbonate oil an obvious confirmation that carboxylic acid was not generated.
(3) The amount of sludge generated by the carbonate oil was significantly less than the ester.
(4) The amount of dissolved iron is less in the carbonate oil than the ester.

While carbonate oil does not generate carboxylic acid, it does generate carbon dioxide in these tests. Tests are currently under way to determine the consequence of the presence of $C0_2$ in real refrigerators as well as the amount actually generated. We are also developing $C0_2$ absorption systems to deal with this issue if it proves to be a problem.

Table 3 Heat Resistance of Oils Tested in Autoclave
(For Refrigerater)

Test Condition Oil / Refrigerant (R-134a)=50 / 50 Temperature x Time : 175°C x 2Weeks

			Carbonate (mod. E-2505)		Ester (Hindered Polyol)	
	Test No.		a-1	a-2	b-1	b-2
Test condition	Water added	(%)	none	0.5	none	0.5
	Air added	(%)	none	0.5	none	0.5
Gas Phase	CO_2	(vol %)	0.09	0.19	0.01	0.05
	Calculated decomposition of carbonate bond(%)		0.19	0.38	—	—
Oil phase	KV (cSt) @40°C	Before testing	30.7	30.7	20.7	20.7
		After testing	30.5	30.2	20.4	20.3
	KV (cSt) @100°C	Before testing	5.80	5.80	4.20	4.20
		After testing	5.78	5.73	4.18	4.13
	Acid Number	Before testing	0.01	0.01	0.01	0.01
		After testing	0.01	0.04	0.34	14.0
	Calculate decomposition of carboxylate bond(%)		—	—	0.08	3.30
	Solved metal in Oil (ppm)	Fe	<1	<1	<1	320
		Cu	<1	<1	<1	<1
		Al	<1	<1	<1	<1
Sludge	Amount		0.3	0.9	0.3	2.8
	Metal defected		—	Fe,Cu,Al	Fe,Cu,Al	Fe,Cu,Al,Ti
Metal catalyst	Change in weight (mg/cm^2)	Fe	0	0	0	-0.5
		Cu	0	0	0	-0.1
		Al	0	0	0	0

Lubricity

The lubricity of the carbonate oil was determined by measuring friction torque, friction coefficient and surface wear under high pressure in an HFC-134a atmosphere. Figure 6 shows the test equipment and test specimens. Test conditions and results are detailed in table 4. Figure 7 and 8 show the metal test specimen surface profile before and after test. These results clearly show the superiority of carbonates to esters. Again, in this test an increase in acid value was noted for the ester system. This test was also conducted with mineral oils in a CFC-12 atmosphere. The results show that the carbonate + HFC-134a system is approximately equal to the mineral oil + CFC-12 system in lubricity.

Our research laboratory is presently evaluating the performance of carbonate oil + HFC-134a in a commercial refrigerator. These tests have been on going for 1 months and to date no problems have been identified.

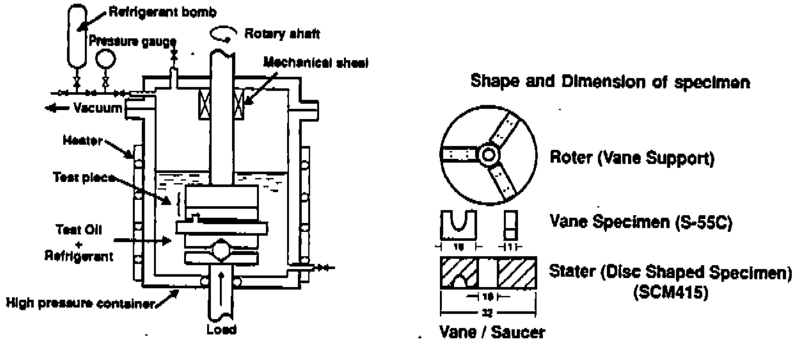


Fig. 6 Friction Testing Machine under High Pressure

Table 4 Lubricity
(Comparison of Oils under the existence of refrigerant)

Test Condition

(1) Equipment : Friction Testing Machine under high pressure
(2) Specimen : Vane (S55C) / Disc (SCM415)
(3) Test Condition : Refrigerant / Oil = 20 / 80 (by weight)
Temperature : 80 °C
Load : 250kg Time : 6hrs. Rotation : 500rpm

Test result

1.Friction and Wear

	Sample		Friction		Wear amount (mg)		
	Oil	Refrigerant	Torque (kg.cm)	Friction coefficiency	Vane	Disc	Total
Current System	Suniso 3GSD	R-12	23.3~26.1	0.09~0.10	1.1	0.1	1.2
New System	mod. E2505	R-134a	15.9~20.6	0.07~0.08	0.9	0.5	1.4
Reference	Ester	R-134a	11.7~21.1	0.05~0.09	92.7	0.1	92.8

2.Deterioration of Oil

Oil	Acid Number (mg-KOH/g)		
	Before Testing	After Testing	Change
Suniso 3GSD	0.00	0.00	0.00
mod. E-2505	0.01	0.01	0.00
Ester	0.02	0.10	0.08

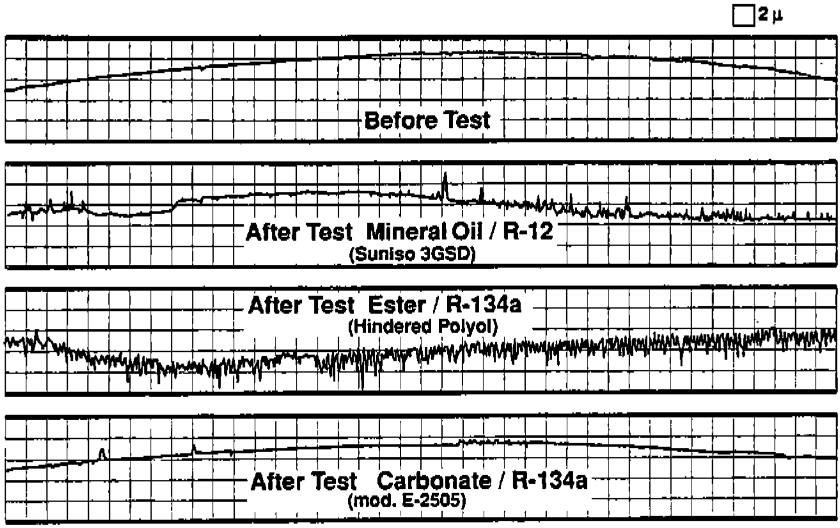


Fig. 7 Profile of vane Metal Surface

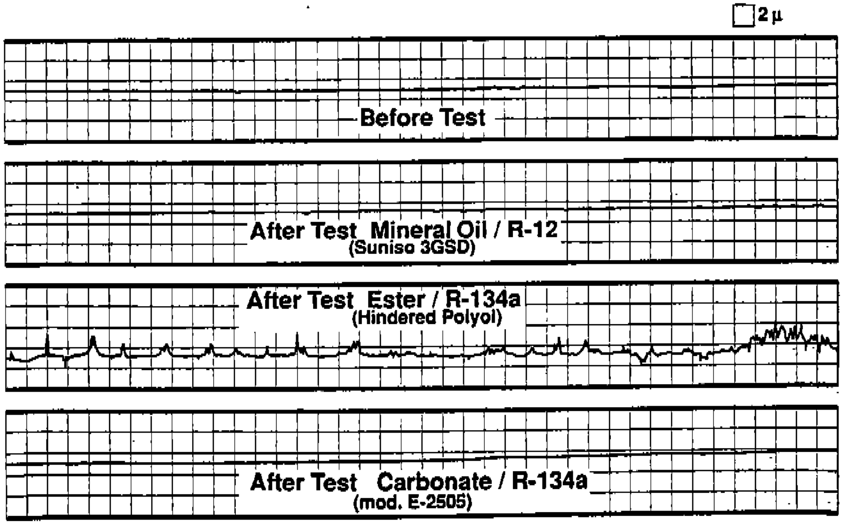


Fig. 8 Profile of Disk Metal Surface

Design Philosophy

The required properties of a base oil for car air-conditioners are lubricity, miscibility with HFC-134a over a broad temperature range, high viscosity index, thermal and chemical stability, non-corrosiveness and compatibility with hose and gasket materials.

In designing a new proper base oil for car air-conditioners, we increased the carbonate group density and the resulting molecular design is shown in Figure 9.

$$R_2\left[\left(PrO\right)_n\!-O-\overset{\displaystyle O}{\overset{\|}{C}}-O-R_1\right]_m$$

R_1 --- C=1~10		
R_2 --- C=2~10	Miscibility Control	
m --- 2~10		
n --- 2~100	Viscosity & Viscosity Index Control	
PrO --- $-CH_2-CH(CH_3)-O-$	Compatibility Control for Other Materials	

Fig. 9 Design Philosophy
(For Car Air Condenioner Application)

Typical Properties

Table 5 shows basic properties of carbonate oils for car air-conditioners. Figure 10 shows the critical solubility curve and Figure 11 shows water absorption curve. These properties verify that the new carbonates, even for high viscosity application, have excellent miscibility, high viscosity index, superior lubricity and less hydrophilic property. Consequently carbonates are an ideal candidate oil for car air-conditioner applications.

Table 5 Typical Properties of Oils for Automotive Air-conditioners
(Comparison between Carbonate and PAG)

Physical properties			Oils				
			Carbonate		PAG		Existing
			M-2310	M-2720	PAG	Mod.PAG	Mineral oil
Viscosity	40°C	cSt	79.4	170	55.8	43.7	90.6
	100°C		13.0	20.0	10.6	9.0	10.9
Viscosity index			165	136	184	193	106
Pour point		°C	-37.5	-30.0	-45.0	-52.5	-20.0
Total acid number		mg-KOH/g	0.01	0.01	0.01	0.01	0.01
Falex value		lbf	790	830	480	670	500
Solubility in R-134a	High-temp.zone	(°C)	+78	+76	+51	+67	Insoluble
	Low-temp.zone		-65↓	-65↓	-65↓	-65↓	Insoluble
Solubility in R-12	High-temp.zone	(°C)	+100↑	+88	+100↑	+100↑	+100↑
	Low-temp.zone		-65↓	-65↓	-65↓	-65↓	-32

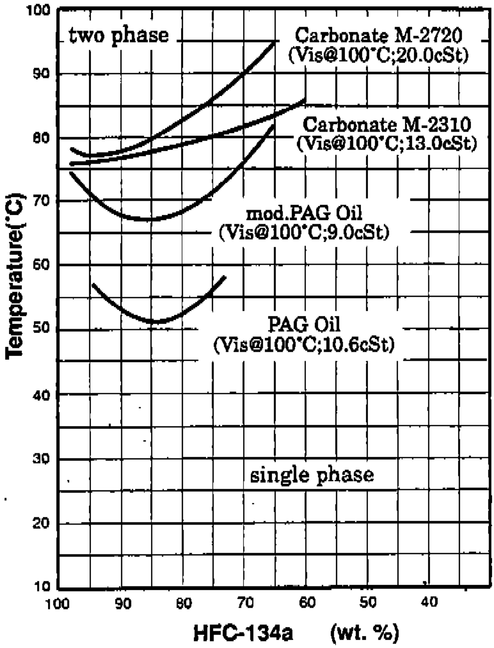


Fig. 10 Critical Solubility Cuves of Oil with HFC-134a

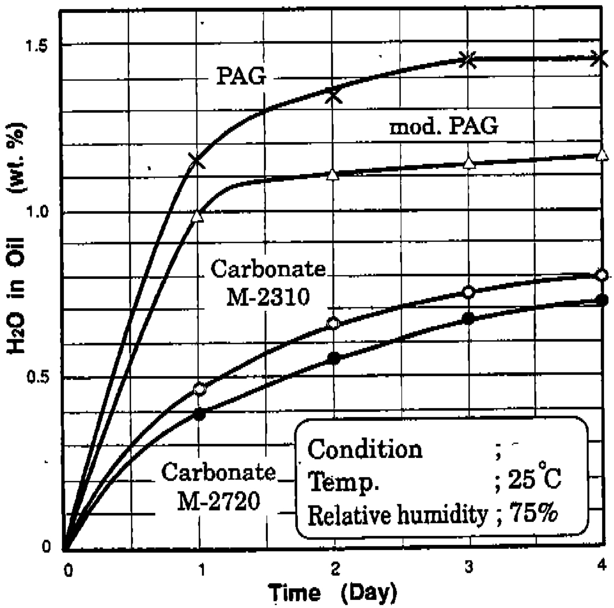


Fig. 11 Water Absorption Curve of oils

Resistance to Heat, Water and Air

Thermal stability tests comparing carbonate oils and PAG's were conducted. 60 grams of oil plus 60 grams of HFC-134a with added water and air were autocraved for two weeks at 175°C. Table 6 shows the superior stability of carbonates to PAG's as measured by acid value, corrosion of metal test strip and color change.

Table 6 Heat Resistance of Oils Tested in Autoclave
(For Automotive Air-conditioners)

Test Condition : Oil/Refrigerant(R-134a)=50/50
Temprature x Time: 175°C, 2 Weeks

	Refrigerant oil	Carbonate		Ester		Mineral Oil	
Condition		A-1	A-2	B-1	B-2	C-1	C-2
	Flon	R-134a		R-134a		R-12	
	Rubber	EPDM		EPDM		NBR	
	Moisture (%)	0.0	1.0	0.0	0.5	0.0	1.0
	Air	Not Present	Present	Not Present	Present	Not Present	Present
Oil	Hue to ASTM						
	Before testing	0.5	0.5	2.0	2.0	0.5	0.5
	After testing	1.0	1.0	3.5	4.0	3.0	4.0
	Total acid number						
	Before testing	0.01	0.01	0.04	0.04	0.01	0.01
	After testing	0.05	0.40	0.59	17	0.18	0.40
Catalyst	Change in appearance	No change		No change	Change	Change	
	Change in weight (mg) Fe	0	0	0	-6	+2	+6
	Cu	0	0	0	-1	+6	+2
	Al	0	0	+1	+2	+1	+1
Rubber	Change in weight(%)	+4.0	+3.9	+6.9	+6.4	-0.9	-1.5
	Change in thickness (mm)	+0.04	+0.04	+0.06	+0.07	-0.55	-0.78
	Change in hardness						
	Before testing	73	71	73	73	75	76

Lubricity

The lubricity of carbonate oils was measured by the Optimol SRV tester. As shown in Figure 12, carbonate oils possess excellent lubricity.

Test Condition

(1) Equipment :Optimol SRV

(2) Specimen :Ball on disk (Sus-2/Sus-2)

(3) Test Conditiom :

Stroke(1mm),Frequency(50HZ)

Load/Time ; 20n/5min.+10min.

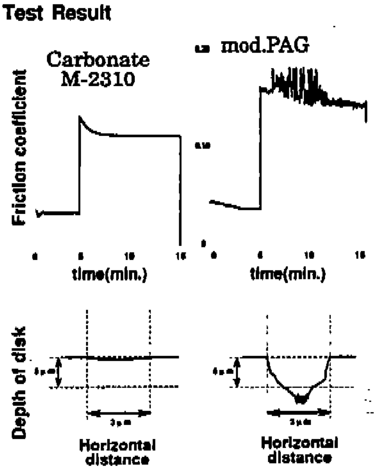


Fig 12. Lubricity
(Comparison of oils under SRV Tester)

CONCLUSION

As evidenced by the above data, the carbonate chemistry provides an excellent base oil for HFC-134a system.

In summary, carbonate oils for refrigerator application offer important advantages over ester oils. They are:

1) Superior lubricity
2) Higher viscosity applications while maintaining HFC-134a miscibility
3) Less hydrophelic property
4) Better wear resistance (non-corrosive)
5) Higher electric resistance

As for the car air-conditioner applications, carbonate oils offer the important advantages over PAG oils. They are:

1) Superior lubricity
2) Excellent miscibility with HFC-134a over a wide range of viscosities
3) Better wear resistance
4) Less water absorption

ACKNOWLEDGEMENT

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