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T. Fukushima
Hitachi Ltds.

M. Kudou
Hitachi Ltds.

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REFRIGERATING OILS FOR ALTERNATIVE REFRIGERANTS

Takashi Kaimai

Kyodo Oil Technical Research Center Co. Ltd.

HFC-134a has been mentioned as a possible replacement for CFC-12 which is a chlorofluorocarbon that has been identified as depleting atmospheric ozone. The major problem of using HFC-134a is the miscibility with conventional lubricants. Some polyglycols are proposed as lubricants for HFC-134a, however which have several defects such as an inadequate miscibility, high hygroscopicity, low electric insulating property, low lubricity and inadequate thermal stability. Therefore, new lubricant for HFC-134a was investigated and the molecule designed ester lubricants have been developed. Also the lubricants for HCFC-123 which can replace CFC-11 are studied.

INTRODUCTION

The remarkable increase in the production and fields of application of refrigerating machines in recent years has been mainly due to the development of the CFC and HCFC refrigerants which have excellent characteristics in terms of safety, stability and noncorrosive property. However, attention has been focused on the issue of the depletion of the ozone layer by chemically stabilized CFC, regulations on CFC were implemented in July 1989 and CFC will be phased out in the future. The use of refrigerants such as CFC-11, CFC-12, etc., is now regulated, which means that we are forced to switch to alternative refrigerants.

In the case of the refrigerating compressor, it is important to select a refrigerating oil suitable for the new refrigerant, as well as to reconsider the design and materials to be used in accordance with for the refrigerator change. This paper summarizes the work on the refrigerating oils for alternative refrigerants.

ALTERNATIVE REFRIGERANTS

The CFC and HCFC refrigerants used in refrigerating equipment are about 45,000 tons, while the percentage ratios of the CFC and HCFC refrigerants used are CFC-11(6%), CFC-12(48%), HCFC-22(43%) and others(3%) in JAPAN. Among these CFC and HCFC refrigerants, CFC-11 is used for centrifugal type refrigerating machines, CFC-12 for automotive air conditioners, household refrigerators, cold storage showcases, etc., and HCFC-22 for room air conditioners, food freezers, etc. The phaseout of CFC in equipment using CFC-11 and CFC-12 refrigerants will mean a reduction in refrigerant loss in the equipment production process, a reduction in the fill quantity, and a switchover to alternative refrigerants.

The alternative refrigerants are shown in Table 1. The HCFC-123 refrigerant may replace the CFC-11 refrigerant, while the HFC-134a refrigerant may replace the CFC-12 refrigerant. Besides these, proposals have been made for the two type mixed refrigerant (HCFC-142b/HCFC-22) and the three type mixed refrigerant (HCFC-22/HFC-152a/HCFC-124 or HCFC-22/HFC-152a/CFC-114). In addition, some of the equipment using the CFC-12 refrigerant will probably switch to the HCFC-22 refrigerant which is not covered by the new regulations.

Table 1 Alternative Refrigerants

	Refrigerants used now	Alternative refrigerants
Centrifugal type refrigerating machines	CFC-11, *	HCFC-123 HCFC-141b
Automotive air conditioners	CFC-12	HFC-134a
Household electric refrigerators	CFC-12	HFC-134a
Cold storage showcases	CFC-12	HCFC-22 HFC-134a

* partially CFC-113, CFC-114

REFRIGERATING OILS FOR HFC-134a

Studies on Basic Materials

The required characteristics on refrigerating oils for the HFC-134a used in automototive air conditioners and household refrigerators, which are major equipment using the CFC-12, are shown in Table 2.

Miscibility of oils with the refrigerant is the basic characteristic from the aspect of oil returning into the compressor. Phase separation of the oil from the refrigerant can cause poor lubrication of the compressor which results in increased wear and decreased compressor life. Previous studies were therefore conducted on the miscibility of the HFC-134a and the various refrigerating oils available on the market. The results are shown in Table 3. The only refrigerating oil that was miscible with the HFC-134a was polyalkylene glycol (PAG), which is a synthetic oil as shown in Table 3 and further studies on PAG have been promoted.

However, the results of studies on PAG have demonstrated that the miscibility with the HFC-134 refrigerant is inadequate especially in the high temperature, while hygroscopicity is high and the antiwear property is inferior compared with the current CFC-12 system. In addition, there are various problematic points such as the fact that electrical insulation is poor. Consequently, basic materials of modified PAG and molecule designed esters have been developed since then.

Table 2 Required Characteristics on Refrigerating Oils for HFC-134a Refrigerant

Characteristic	Use	Automotive air conditioners	Household refrigerators
Viscosity	Swash plate or recipro. Rotary	10 cSt @ 100°C 20 cSt @ 100°C	15-32 cSt @ 40°C 32-56 cSt @ 40°C
	High temp Low temp	>80°C <-20°C	>80°C <-40°C
Stability	HCFC-134a CFC-12	Same * Same *	Same * Same *
	Lubricity	Same *	Same *
Hygroscopicity		Low	Low
Copper plating		Same *	Same *
Volume resistivity * *		—	> 10 ¹²
Compatibility with organic materials		Same *	Same *

- * Comparison with CFC-12 refrigerant-mineral oil system.
- ** Electrical insulating property.

Table 3 Miscibility of HFC-134a with Various Refrigerating Oils

Type of oil	Phase separation temperature (°C) (oil/HFC-134a - wt%)			
	1/9	2/8	4/6	8/2
Paraffinic oil	Immiscible	Immiscible	Immiscible	Immiscible
Naphthenic oil	"	"	"	"
Aromatic oil	"	"	"	"
Alkyl benzene	"	"	"	"
Ester	"	"	"	-9
PAG	High temp.	75	67	71
	Low temp.	<-50	<-50	<-50

Note: Commercially available oils (VG32) were tested.

Refrigerating Oil for Automotive Air Conditioners

The characteristics of refrigerating oils for automotive air conditioners are shown in Table 4. In the case of automotive air conditioners, the phase separation temperature should be high when the compressor is started during the hot summer season. In other words, the refrigerant with a large specific gravity becomes the lower layer when the refrigerant and oil are separated at high temperature. It becomes a lubrication by only the refrigerant of lower layer at the start of compressor and there might be the danger of a seizure.

Experimental oil C with modified PAG as the basic material and experimental oil D with ester as the basic material have excellent characteristics in this respect. In addition, experimental oil D has a low hygroscopicity, while the lubricity is also good. Moreover, it also has excellent characteristics in terms of stability when the CFC-12 refrigerant is contaminated.

Table 4 Characteristics of the Refrigerating Oils for Automotive Air Conditioners (Swash plate)

Oil Material type		A	B	C	D	Required value
		PAG-1	PAG-2	Modified PAG	Ester	
Viscosity (cSt)	40°C	56.1	49.3	51.3	78.8	—
	100°C	10.8	10.2	9.8	10.3	10
Viscosity index		187	201	179	114	—
Phase separation temperature, °C						
	High	46	69	80	>80	>80
	Low (oil/HFC-134a=2/8)	<-50	<-50	<-50	<-50	<-20
Saturated moisture content (25°C) ppm		26,000	21,000	24,000	1,500	—
Solubility with mineral oil		In- soluble	In- soluble	In- soluble	Soluble	—
Sealed tube test (Colour, ASTM)						
	0 days	L 0.5	L 0.5	L 0.5	L 0.5	
	10 days	L 0.5	L 0.5	L 0.5	L 0.5	
	20 days	L 0.5	L 0.5	L 0.5	L 0.5	
	175°C, Fe, Cu, Al					
Sealed tube test (Colour, ASTM)						
	3 days	> 8	> 8	> 8	L 1.0	
	6 days				L 1.0	
	10 days				L 1.0	
	175°C, Fe, Cu, Al					
Falex * extreme pressure 60°C, (Fe/Fe)						
	Lbf	860	880	950	1020	
Falex * wear test (pin/block)						
	300Lbf, 1Hr	15/1	10/1	6/1	3/1	
	mg					

* Material : Fe pin SAE 3135
Fe block AISI 1137

Note ; PAG-1 RO(PO)_n H
PAG-2 RO(PO)_n R
Modified PAG O₀
RCO(PO)_n CR

This paper has so far given an outline on refrigerating oils for HFC-134a. At present, it can be considered that the ester type is superior overall. The properties of the various oils in comparison with mineral oil are shown in Table 7.

Table 7 Properties of the Various Refrigerating Oils for HFC-134a

Properties	Oil	P A G	Modified	Ester	Mineral oil (CFC-12)
		P A G	P A G		
Stability	HFC-134a	○	○	●	—
	CFC-12	X	X	●	○
	Oxidation	X	X	●	○
Mutual solubility	High temperature	X	△	●	●
	Low temperature	●	●	○	○
Lubricity	Iron / Iron	X	△	○	○
	Iron / Non-ferrous	X	△	○	○
Hygroscopicity		X	X	○	●
Copper plating		X	X	○	●
Electrical insulating property		X	△	○	●

● : Excellent ○ : Good
 △ : Moderate X : Bad

REFRIGERATING OIL FOR HCFC-123

The CFC-11 has mainly been used by the centrifugal type refrigerating machines. It has therefore become necessary to study the possibilities of alternative refrigerants due to the new regulations on the CFC-11. The HCFC-123 is a promising candidate as alternative refrigerant, so studies have been conducted on refrigerating oils for the HCFC-123.

Paraffinic mineral oils have mainly been used for the CFC-11 in JAPAN, so an evaluation was made using the present paraffinic mineral oils and results are shown in Table 8. Since the number of Cl in the molecule is 2 in the case of the HCFC-123 (3 in the case of the CFC-11), it offers advantages in term of stability. Furthermore, as a result by the sealed tube test, the stability when using the HCFC-123 refrigerant was drastically improved in comparison with the case of the CFC-11. In addition, there was no problem associated with the solubility of the refrigerant and oil.

From the facts stated above, the present paraffinic mineral oils can be used as the refrigerating oils for the HCFC-123.

Table 8 Evaluation of Refrigerating Oils for HCFC-123

Properties		Oil	Paraffinic mineral oil		
			VG 56	VG 68	
Viscosity	40°C		57.5	65.6	
	cSt	100°C	8.00	8.69	
Viscosity index			106	105	
Pour point, °C			-30.0	-30.0	
Phase separation temp. (°C)		Oil : HCFC-123			
	1 : 9		-40	-39	
	2 : 8		-39	-38	
	4 : 6		-38	-38	
	6 : 4		-38	-37	
	8 : 2		-37	-37	
Sealed tube test *		HCFC-123	CFC-11	HCFC-123	CFC-11
Colour	0 days	L 1.0	L 1.0	L 1.0	L 1.0
(ASTM)	3 days	L 3.0	>8	L 3.0	>8
175°C	6 days	L 5.0		L 5.0	
	10 days	>8		>8	

* Cat.; Fe, Cu, Al

CONCLUSION

As refrigerating oils for HFC-134a refrigerant PAG, modified PAG and the molecule designed ester were studied and it was ascertained that ester had excellent characteristics, from the view point of miscibility with refrigerant, hygroscopicity, electric insulating property, lubricity and thermal stability. The performance tests by actual compressor have been carried on by compressor manufacturers.

Paraffinic mineral oils can be used as the refrigerating oils for HCFC-123 refrigerant, which is a possible replacement for CFC-11.