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Study of Technology for Refrigerant Applications 1

T. Iizuka
Hitachi

A. Ishiyama
Hitachi

H. Hata
Hitachi

T. Sugano
Hitachi

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1. Materials Compatibility for HCFC-22 Alternative Refrigerants

Tadashi Iizuka, Akihiko Ishiyama, Hiroaki Hata and Tsuneji Sugano

Hitachi, Ltd.

Abstract

HFC-32, HFC-125, HFC-134a and their blends are considered to be promising HCFC-22 alternative refrigerants, which will be used for refrigerators, air conditioners, and other refrigeration applications. The materials compatibility of several basic materials were examined. Some of them can be used without modifications; however, the drop-in tests showed that some problems remain to be sorted out for the practical use.

Introduction

To meet the environmental demands, CFCs and HCFCs used as refrigerant in refrigeration systems should be replaced by HFCs. HFC-134a, HFC-32/134a binary blend and HFC-32/125/134a ternary blend are the primary candidates for the alternative refrigerants. According to the minimum bond dissociation energies of HCFC and HFC molecules listed in Table 1 *(1)*, all HFCs are thermally more stable than HCFC-22.

In this paper, the compatibility of refrigeration lubricants and materials used for compressors and refrigeration systems were examined.

Basic Materials

The basic materials for rotary compressors and their associated properties are shown in Figure 1. To satisfy the reliability of refrigeration systems, the compatibility of these basic materials should be as good as that of current HCFC-22 system. If the compatibility is not satisfied, certain modification of compressors or system design will be required.

Refrigeration Lubricants

(1) Solubility and miscibility

Both solubility and miscibility of refrigerant in refrigeration lubricant play an important role in especially lubrication of compressor parts. For example, higher solubility leads the dilution of lubricant and lower miscibility causes poor oil return into the compressor. As shown in Table 2, certain polyolesters (POE) and polycarbonates have good miscibility with HFCs. The lower critical soluble temperature (LCST) of lubricants in HFC-32, HFC-134a, HFC-32/134a and HFC-32/125/134a are summarized in Figure 2.

(2) Stability

The results of sealed tube test of POE E1 and polycarbonate C1 in HFCs are shown in Table 3. In the POE E1, a little decomposition of refrigerants was observed. Although the decomposition of refrigerants in C1 is vary small, a very large amount of carbon dioxide was formed in the polycarbonate C1 due to the decomposition of polycarbonate C1. A small amount of CFC-115 was included in HFC-125 but no significant effects were observed. On the other hand, CH_3Cl in HFC-32 caused slight color change over the surface of iron catalyst.

Hydrolysis of polyolesters and polycarbonates

Since the hydrolysis and the esterification are an equilibrium reaction, shown in the equation (1), when there is water available in the POE system, POE can be hydrized into carboxylic acid and alcohol.

$$R_1COOR_2 + H_2O \rightleftarrows R_1COOH + R_2OH \qquad (1)$$

Because one molecule of water produces one molecule of carboxylic acid, the final total acid number (TAN) after the complete hydrolysis can be estimated by following equation (2).

$$\text{TAN (mgKOH/g)} = 0.0031 \times \text{Water Content (ppm)} \qquad (2)$$

where no acids formation other than hydrolysis is assumed.

In order to maintain low TAN, several methods were proposed. For example, use of dryer to remove residual water in the system, addition of epoxy-type acid catcher to eliminate acids formed and preparation of hydrolytically stable POEs. All methods are proved to be effective. In figure 3, the relationship between the initial water content and the final TAN are shown along with the content of acid catcher. For instance, the final TAN of trimethylolpropane (TMP) ester E1 with acid catcher showed 1/50 lower TAN of pentaerythritol (PE) ester E5.

The final TAN of polycarbonate C1 is ca. 1/10 of E1. This is because no carboxylic acid is formed through the hydrolysis of polycarbonate shown in below.

$$R_1O\underset{\underset{O}{\|}}{C}\text{-}OR_2 + H_2O \longrightarrow R_1OH + R_2OH + CO_2 \qquad (3)$$

We'd like to point out here that the strict control of water and contaminants is essential to maintain low TAN and low lubricant degradation.

Motor Materials

(1) Insulation Film

In Figures 4 and 5, the results of the sealed tube test for insulation film are shown. The amount of oligomer extracted from polyethyleneterephtharate (PET) film is the largest in HCFC-22/mineral oil system compared with other HFC/POE systems. In the case of HFC blend, the amount of oligomer extracted lie between in single HFC components. Also the tensile strength of PET film was remained better in HFC/POE systems than in HCFC-22/mineral oil system. So the insulating film used for the current HCFC-22 system has adequate properties in HFC/POE system also.

(2) Magnetic Wires

In Table 4, the results of sealed tube test for magnetic wires are shown. As like as the insulating film, the current magnetic wire, the modified esterimide / polyamideimide double coated wire, is suitable for HFC/POE systems.

Molecular Sieves

To maintain low water concentration in the refrigeration systems, the choice of suitable Molecular Sieves (named by the UOP) for a dryer is very important. In Table 5, several types of Molecular Sieves with different pore sizes were compared *(2)*. The DSC diagrams of water and HFC-32 desorption from Molecular Sieves XH-9 and XH-10C (a developmental Molecular Sieves) are shown in Figure 6. This clearly shows that XH-9 adsorbs both water and HFC-32 molecules. The higher desorption temperature of HFC-32 from XH-9 than that of water from XH-9 suggests that XH-9 has a tendency to adsorb pure HFC-32 stronger than pure water. Moreover XH-9 has lower selectivity for water adsorption in HFC-32 than XH-10C. On the other hand, XH-10C has superb ability for both selective adsorption of water and maintain higher mechanical strength. Currently we are examining its characteristics in detail for practical use.

Conclusions

The materials compatibility for HFC systems was examined and we figured out that;

(1) TMP ester with epoxy-type acid catcher has both good miscibility with HFCs and improved hydrolytic stability.

(2) Current motor materials for insulating film and magnetic wires used for HCFC-22 system can be used in HFC systems without modification.

(3) Developmental Molecular Sieves XH-10C is the best choice of the desiccants tested for a dryer at low temperature side of HFC-32 based refrigerant systems.

(4) Drop-in test using above materials was carried out and it is found out that the reliability of system was satisfactory in HFC systems.

References

1. David A Dixon, Du Pont Tech. Data Experimental Bond Energies, Sep.3, 1993.
2. Alan P Cohen, Compatibility of Desiccant with Alternative Refrigerants, Feb.1993.

Table 1 Alternative Refrigerants for HCFC22

Refrigerant	HCFC22	HFC125	HFC134a	HFC32	HFC32/134a (30/70wt%)	HFC32/125/134a (23/25/52wt%)
Chemical Structure	$CHClF_2$	CF_3CHF_2	CF_3CH_2F	CH_2F_2	CH_2F_2/ CF_3CH_2F	CH_2F_2/CF_3CHF_2 $/CF_3CH_2F$
Minimum Bond Strength(KJ/mol)	357 CHF_2-Cl	385 CF_3-CF_2H	394 CF_3-CFH_2	423 CF_2H-H	—	—
ODP	0.05	0	0	0	0	0
GWP	0.34	0.84	0.25	0.13	0.21	0.37
Flammability	no	no	no	moderate	marginal	no

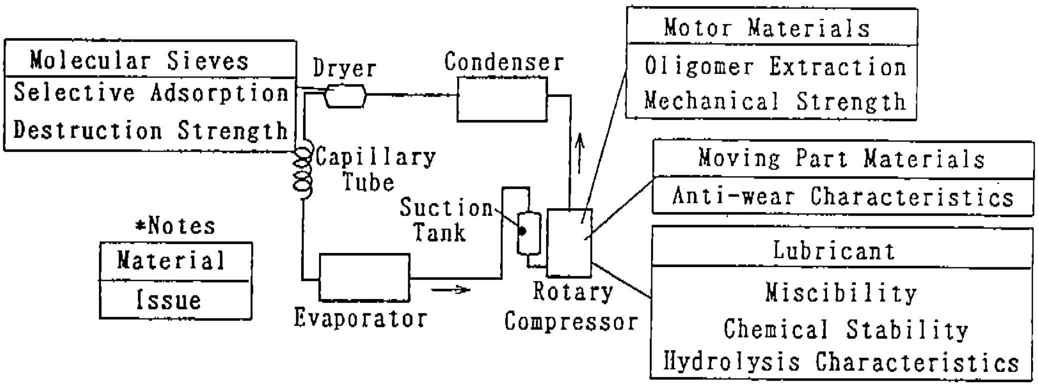

Fig.1 Schematic Figure of a Refrigeration System

Table 2 Esters and Carbonates

Oil	Base Oil	Viscosity (mm^2/s) 40℃	Viscosity (mm^2/s) 100℃	Pour Point(℃)	Critical Soluble Temp. (℃) HFC32	Critical Soluble Temp. (℃) HFC125	Critical Soluble Temp. (℃) HFC134a
E1	trimethylolpropane/ i-Cn acid ester	31	5	< -40	15	-45	-43
E2		56	8	< -40	> 20	-20	-15
E3	pentaerythritol/ i-Cn acid ester	31	5	< -40	> 20	< -80	-36
E4		56	8	< -40	> 20	< -80	-29
E5	pentaerythritol/ i-Cn,n-Cn acid ester	30	5	< -40	-24	< -80	-70
E6		56	8	< -40	8	< -80	-47
E7	neopenthylglycol/dibasic acid/i-Cn acid ester	34	6	< -40	-18	< -80	< -70
E8		52	7	< -40	- 5	< -80	< -70
C1	carbonate	30	6	< -40	> 20	< -80	-20
C2		56	8	< -40	-65	< -80	< -60
M1	naphthenic mineral oil	56	6	< -40	> 20	> 20	> 20

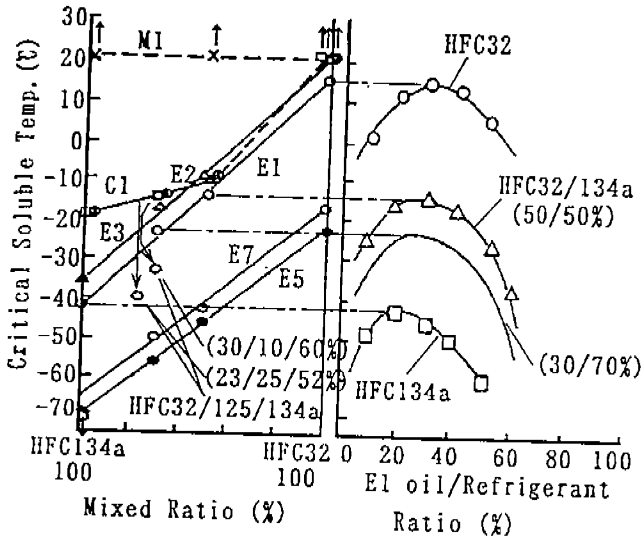

Fig.2 TAN Change by Hydrolysis and Effect of Epoxy Additive

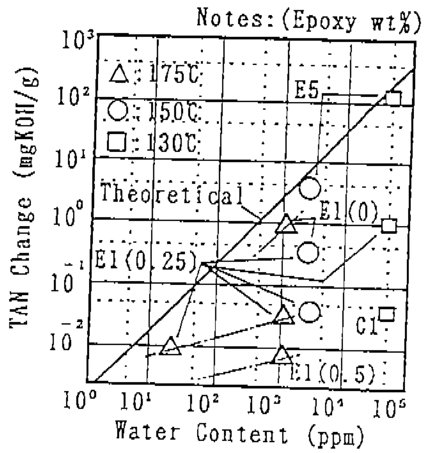

Fig.3 TAN Change by Hydrolysis and Effect of Epoxy Additive

Table 3 Result of sealed tube test for ester and carbonate
Oil/refrigerant = 1:1, 200℃, 40 days

Lubricant		Ester E1			Carbonate C1		
Refrigerant		HFC134a	HFC32	HFC125	HFC134a	HFC32	HFC125
Refrigerant Composition (wt%)	HFC134a	99.997			99.997		
	HFC32		99.994			99.994	
	HFC125			99.212			99.216
	HFC134	0.003			0.003		
	HFC1123						
	HFC41					0.002	
	CH_3Cl		0.006			0.005	
	CFC115			0.788			0.784
	HCFC124a			0.001			
	HFC1114						
Others (area%)	CO_2	0.007	0.008	0.529	11.482	9.997	11.387
	Hydrocarbons	0.025	0.013	0.025	0.407	0.339	0.372
Oil Color (ASTM)		1(-)	1(-)	1(-)	1(-)	1(-)	1(-)
Change of Metal Catalysts	Fe	neg.*	neg.*	none	none	none	none
	Cu	none	neg.*	none	none	none	none
	Al	none	none	none	none	none	none

*neg.:negligible

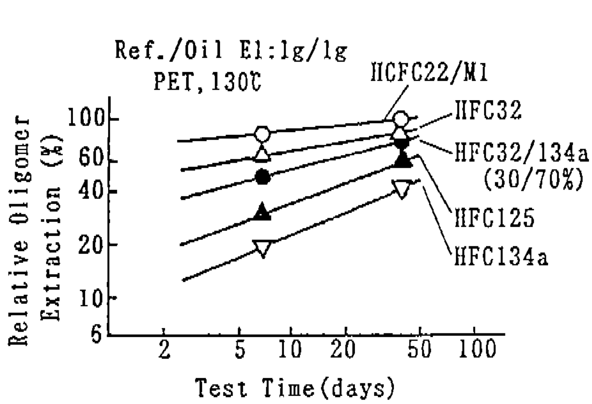

Fig.4 Oligomer Extraction from Insulating Film

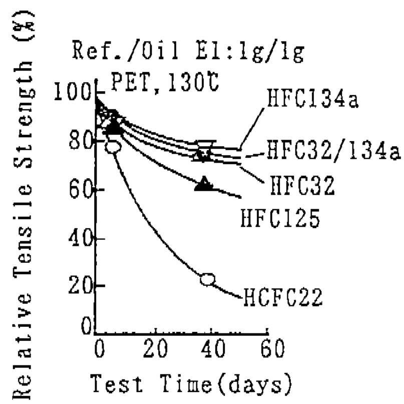

Fig.5 Tensile Strength Change of Insulating Film

Table 4 Result of Sealed Tube Test for Magnetic Wire

Refrigerant	—	HFC125		HFC32		HFC134a		HCFC22	
Lubricant	E1	E1		E1		E1		M1	
Test Days	initial	7	40	7	40	7	40	7	40
Crazing ability	OK	OK	OK	OK	OK	OK	OK	OK	OK
Pencil hardness	6H	6H	6H	6H	6H	6H	6H	6H	5H
Winding ability	OK	OK	OK	OK	OK	OK	OK	OK	OK
Blister	none	none	none	none	none	none	none	none	none
Relative BDV* (%)	100	96	108	92	98	92	93	94	96

*BDV:Break Down Voltage

Table 5 Compatibility of Molecular Sieves with HFCs

Molecular Sieves			4A-NRG	XH-5	XH-7	XH-6	XH-9	XH-10C
Pore Diameter(Å) approx.			4	4	3	3	3	3
Refrigerant /Molecular size(Å)	HFC125	4.2	good	good	good	good	good	good
	HFC134a	4.2	NG	NG	good	good	good	good
	HCFC22	3.8	NG	NG	NG	good	good	good
	HFC32	3.3	NG	NG	NG	NE*	NE*	good
	H_2O	2.8	—	—	—	—	—	—

*NE:Not Enough Selectivity

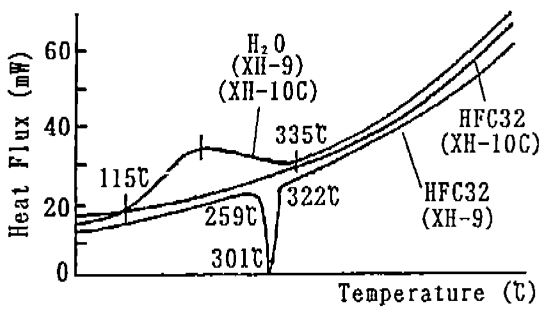

Fig.6 DSC Diagram of Molecular Sieves