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DEVELOPMENT OF COMPRESSOR MATERIAL TECHNOLOGY FOR HFC134a USE

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ABSTRACT

HFC134a was selected for the alternative refrigerant for CFC12 because of its excellent properties like thermodynamics. But there were several problems like immiscibilitiy with oil to replace CFC12 by HFC134a. In order to solve these problems, we developed new polyol ester refrigeration oil which had good miscibility with HFC134a and excellent thermal stability and lubricity as well. To apply polyol ester oil into refrigeration system, we evaluated compatibility with insulation materials and develop contamination control technology to reduce sludge deposition in system. In this paper we introduce newly developed polyol ester oil and its properties, material technology and chemical specifications in refrigeration system for HFC134a use.

INTRODUCTION

Selection of Refrigerant and Refrigeration Oil

Refrigerants as shown in Table 1[1]were the alternative candidates for CFC12. HFC134a was selected for domestic refrigerator's refrigerant because of its thermal properties, non-flamability and zero ODP.[2] But HFC134a is not miscible with conventional mineral oil and synthetic oil. Table 2[1][3]shows comparison of several typical lubricants on properties. PAG oil was evaluated at first stage of development, but its electrical insulation resitivity was poor and not acceptable for hermetic compressor that has a motor in it. Thus our target of development has been shifted to polyol ester oil.[4]

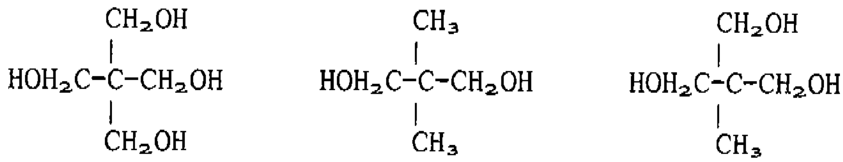
Problems in HFC134a/Ester Oil System

HFC134a has no chroline in its structure, so it tends to increase wear of sliding parts of compressor. As shown in Fig.1[5], system with HFC134a and polyol ester oil has tendency to produce sludge like metal salt caused by hydrolysis and oxidation of polyol ester oil and its tendency is accelerated by process contamination. Produced sludge might be root cause of capillary blockage and drop of the capacity. Therefore we had to develop appropriate refrigeration oil that has good lubricity and thermal stability as well.

DEVELOPMENT OF POLYOL ESTER OIL

Raw Materials of Ester Oil

We started to select the appropriate base oil in hydrolysis property. Hinderd type of polyol ester has been used as various kinds of lubricants. Properties of hinderd ester vary according to types of multivalent alcohol and fatty acid, as raw materials of hinderd ester. Pentaerythritol (PET), Neopentylglycol (NPG) and Trimethyrolpropane (TMP) are popular hinderd types of alcohol. Each structure are as shown below,



PET NPG TMP

Table 3 shows comparison of each alcohol stability. PET and NPG are superior to TMP in hydrolytic stability. Table 4 shows comparison of acid structure on stability, and branched type acid is superior to linear type acid. We chose PET and NPG as raw alcohol and branched acid as raw acid to our base oil.

Choice of Additives for Stability

Hydrolysis inhibitors and oxidation inhibitors have been investigated, and the best combination of them was chosen. Fig.2 shows comparison of ester oil with and without inhibitors by sealed glass tube test. The effect of additives is ascertained, and we decided to use these inhibitors.

TRIBOLOGY TECHNOLOGY FOR NEW SYSTEM

Self lubricating effect by chroline atom can not be expected for HFC134a, because there is not any chroline atom in HFC134a molecule. Therefore lubricating ability of ester oil with HFC134a is inferior to that of mineral oil with CFC12. Table 5 shows the result of Amsler wear test comparing ester oil with and without Tri-Cresyl Phosphate (TCP). By using TCP the wear of test pieces dramatically reduced, and Total Acid Number (TAN) of tested oil was kept at low level as well.

In addition, we introduced phosphate surface treatment on piston and crankshaft to improve the wearability.

MATERIAL COMPATIBILITY STUDY

Both HFC134a and ester oil have strong polarities, and influence on organic materials in the system is greater than that in CFC12/mineral oil system. Therefore we investigated material compatibility for polymeric materials used in compressor and changed materials as shown in Table 6. High heat-resistant enameled wires such as theic polyester wire overcoated with amideimide can be used for HFC134a application. The conventional polyester wire overcoated with nylon cannot be used due to degradation by HFC134a. Concerning insulation film, we introduced low oligomer film, because the oligomer extractability of HFC134a is greater than that of CFC12.

CONTAMINATION CONTROL FOR RELIABILITY

Some sludge was found in refrigeration cycle after durability test at the first stage of this development. By analyzing this sludge, metal salt was found and it proved that degradation of ester oil occurred as shown in Fig.1. As a result of fundamental experiment as shown in Fig.3[5], moisture and residual air in the system accelerate degradation of ester oil. Therefore residual moisture and residual air in refrigeration cycle should be controlled strictly at low level.

We also investigated stability of flux, process oil and cleaning agents which are used in manufacturing process and chose agents which had less influence on stability. Fig.4 shows a result of investigation about influence of flux on stability. No.C is better flux on stability and decrease decomposition of ester.

CONCLUSION

Compressor for refrigerator with HFC134a has been developed based on the above mentioned material technology. And we have having good reputation in both property and reliability of our compressor. Key technology of this development was summerized below.

(1) Choice of high stability base oil and appropriate additives.
(2) Improvement of wearability adopting surface treatment on sliding parts.
(3) Introduction of the appropriate organic materials.
(4) Choice of auxiliary materials which have little influence on stability of HFC134a/ester oil system.
(5) Strict contamination control on residual moisture, residual air and so on.

ACKNOWLEDGEMENT

We wish to express our sincere thanks to oil and other material companies related to this development.

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Table 1. Properties comparison of alternative refrigerants

Item \ Refrigerant	HFC 134a	HCFC 22	HCFC Blend	CFC 12
Structure	CF_3CH_2F	$CHClF_2$	22/152a/124	CCl_2F_2
Boiling point (°C)	-26.2	-40.8	-28.0	-29.8
ODP	0	0.055	0.03	1.0
GWP	0.25	0.36	0.22	3.0
Flamability	none	none	none	none
Refrigeration properties (comparison with CFC 12)				
Capacity ratio	0.96	1.59	1.09	1.0
Efficiency ratio	0.96	0.96	1.00	1.0

Table 2. Properties comparison of various lubricants

Item \ Lubricants	Polyol ester	PAG	Mineral oil	Alkyl benzen
Miscibility with HFC 134a	+ +	+ +	−	−
Lubricity	+	+	+ +	+
Thermal stability	+	+	+ +	+ +
Compatibility with polymer	+	+	+ +	+ +
Electric insulation	+ +	−	+ +	+ +
Hydrolysis	+	+	+ +	+ +
Hygroscopicity	+	+	+ +	+ +

[+ + ; good] [+ ; Conditionally good] [− ; poor]

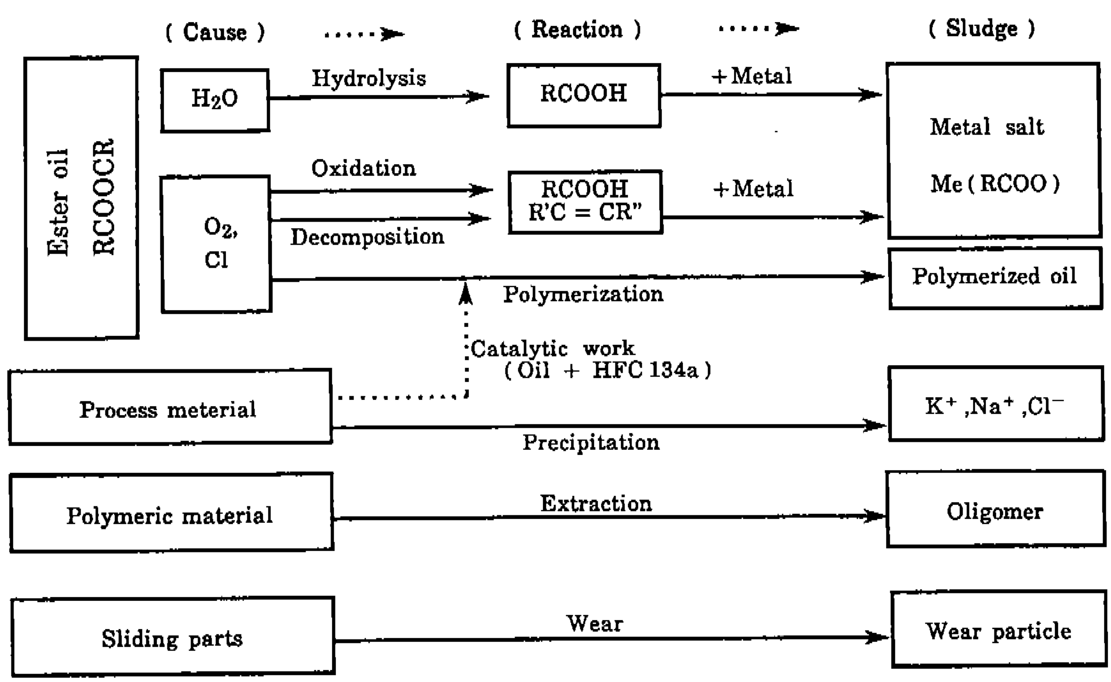

Fig.1 Mechanism of sludge formation

Table 3. Comparison of raw alcohol type on stability

TAN of oil (mg KOH/g)

Duration \ Alcohol	TMP	NPG	PET
7days	0.07	0.01	0.01
14days	0.43	0.02	0.02
28days	1.95	0.02	0.06

Note : (1) Sealed glass tube test at 175°C
(2) Raw acid type are Branch C_7~C_8
(3) TAN stands for total acid number.

Table 4. Comparison of raw acid structure on stability

Oil	Structure		TAN of oil (mg KOH/g)
	Alcohol	Acid	
A	PET	Linear C5	0.03
B	PET	Linear C5.C6	0.04
C	PET	Branch C7.C8	0.01
D	PET and NPG	Branch C8	0.01

Note : (1) Glass tube test under air ambient

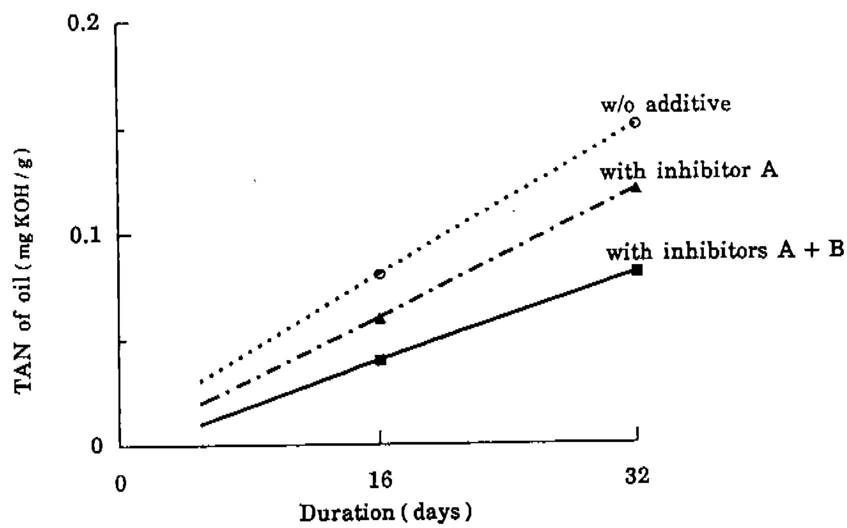

Fig.2 Effect of additives on stability of oil (Sealed glass tube test at 175℃)

Table 5. Effect of additive on wear by Amsler wear test

Oil	Wear width of fixed TP (mm)	O.D.reduction of rotating TP(μm)	Amount of sludge (mg)	TAN of oil (mg KOH/g)
With TCP	0.25	− 1	7.2	0.02
W/O TCP	0.65	− 4	23.6	0.11

Table 6. Comparison of materials between CFC12 and HFC134a use

Parts \ Refrigerant	CFC 12	HFC 134a
Magnet wire	PE / Nylon	E I / AI Theic PE / AI
PET film	General type	Low oligomer type
PBT muffler	General type	Low oligomer type
Piston	No treatment	Phosphate treatment

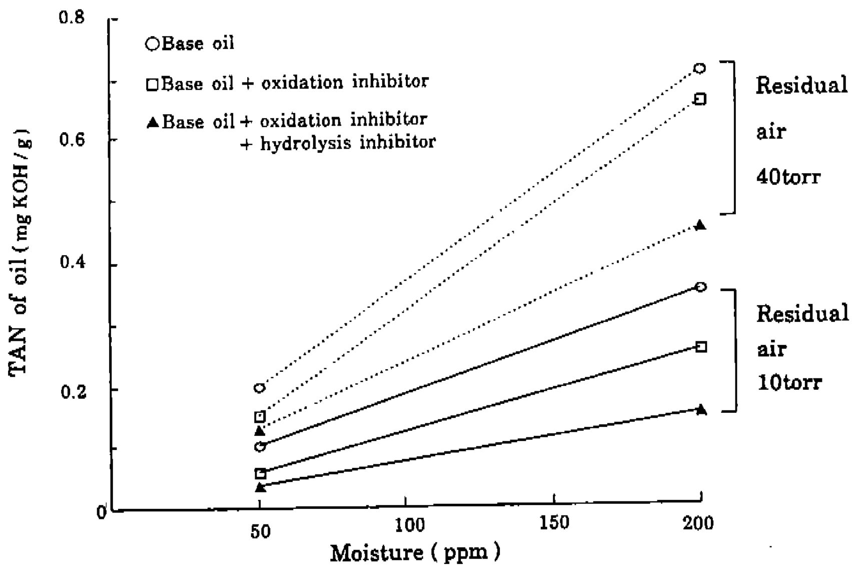

Fig.3 Oil degradation by air and moisture

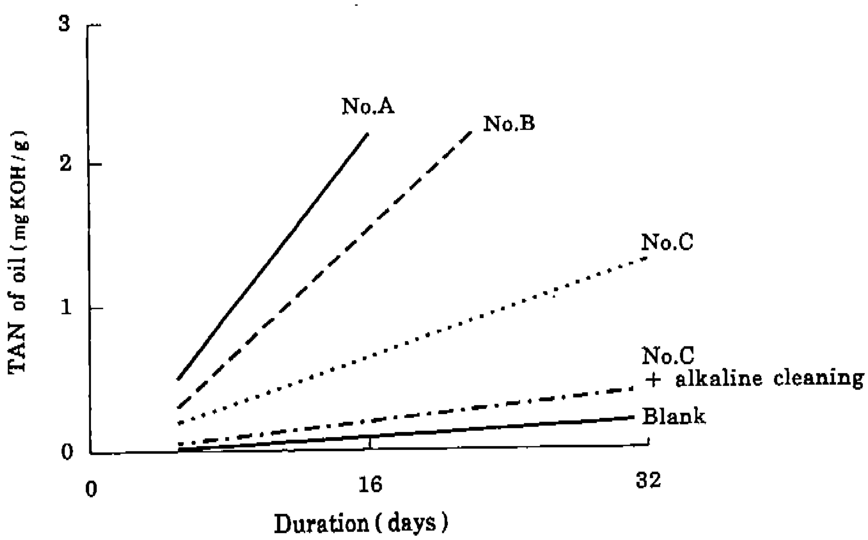

Fig.4 Influence of brazing flux on stability of HFC134a/ester oil (Sealed glass tube test at 175℃)