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ABSTRACT

In replacing CFC-12 with HFC-134a for refrigerator compressors, the compatibility with lubricating oil, and lubrication in general, are of major concern. HFC-134a does not have adequate solubility with current lubricating oils because of its molecular structure. Current oils also do not provide enough lubricating action when using HFC-134a. A new oil and new materials have to be utilized in order to use HFC-134a.

Developing a new lubricating oil involved numerous tests of different combinations of many polyolester synthetic oils and additives. One of the pre-evaluated methods was pursued via sealed tube tests. Lubricated parts were selected by studies involving a plane-on-roller type of wear test machine and by analyzing the traces of acid material commonly created during the lubricating action.

The matrices of new lubricating oils and new lubricated materials were estimated based on durability tests conducted on compressors and refrigerators. Results showed that polyolester synthetic oils having a low total acid value and including certain quantities of additives did not break down into a tar-like substance and they did not produce composite particles in the operating compressors and refrigerators. The study also found that ceramics and anti-corrosion alloy steel possessed good abrasion-reducing qualities.

Based on our evaluation, we will implement compressor reliability tests and apply HFC-134a to rotary compressors for refrigerators.

1. Introduction

The issue of chlorofluorocarbons triggered by the problem of destruction of the ozone layer is now in the stage of finishing the selection of substitutes by material makers and the measurement of basis properties of candidate substitutes at university and other institutes[1)]. In particular, as the substitute for CFC-12 which has been widely used in the small-sized refrigerating systems such as refrigerators and freezers, HFC-134a is reputed to be most suited. It is because the HFC-134a is very close to the current CFC-12 in its thermodynamic characteristics. Actually, however, only by replacing the refrigerant, the refrigerating performance is slightly lowered, which is confirmed by manufacturers including us[2),3)]. It is hence attempted to attain the conventional performance by improving the capillaries, optimizing the refrigerant amount, upgrading the compressor, or the like.

Among such considerations, what is most important is to keep the reliability for a long period. Above all, concerning the compressor which is the heart of the refrigerator, since it is used for nearly ten years in average in various conditions ranging from high temperature to low temperature, it has been an essential subject to keep the reliability when the refrigerant is replaced.

In Japan, especially, rotary compressors of small size and low noise level noted for high pressure and high temperature atmosphere within the shell are widely used due to the restrictions of noise pollution and installation area of refrigerator. The results of durability test in the rotary compressor are reported below.

HFC-134a, a candidate substitute, is high in polarity as compared with the conventional CFC-12 because F atoms are shifted to one side of the molecular structure, and hence it is not dissolved in widely used mineral oil or alkylbenzene oil. Accordingly, as the oil of high solubility, glycol oil and ester oil were introduced by oil manufactures[4)]. Particularly, in the hermetic compressor incorporating an electric part of motor, the electric insulation is very important, and the ester oil of high volume resistivity and low dielectric constant was chosen. Besides, the HFC-134a does not contain Cl atoms unlike the CFC-12, and is hence inferior in lubricity, and it is said that the wear resistance is particularly different in the extreme-pressure state.

2. Development and improvement of materials

2.1 Comparison of oil and improvement of additive

Polyol-ester is classified into hindered ester, complex ester, polycarbonate ester, and others, according to the starting material and the synthesizing process. In the hindered ester, the structure of the carboxylic acid side is varied and diversified, and its solubility with HFC-134a is known to vary significantly depending on the size of molecular weight, the linearity of structure and the side chain of alkyl group.

In the present study, points of investigations were first narrowed down to the lubricity of oil, and the abrasion between the vane and roller in which the lubricating condition is most severe in the rotary compressor was studied. The lubrication between vane and roller is a linear contact, and it is said to be usually close to boundary lubrication. At our company, in the plane-on-roller abrasion test having a structure very close to this lubrication form (Fig. 1), the condition near to the boundary lubrication was reproduced by varying the oil feed method, load and sliding speed. In the present study, too, in order to see the effects of refrigerant, the lubricating chamber was filled with HFC-134a or CFC-12 atmosphere in order to evaluate by comparison. The results of metal surface state are shown in Fig. 2.

The results of various type of esters are shown in first line of Table 1. Among ester oils, difference in lubricity due to structural difference was not clear. In severe conditions such as boundary lubrication, the adsorption of ester group of high polarity on the metal surface occupies a large factor in lubrication, and it may be considered because the contribution of the size of molecular weight of the structure of alkyl group is small. These findings, however, did not coincide always with the failure load of FALEX, and therefore the seizure phenomenon at high load should be considered differently from the abrasion phenomenon at low load occurring in the compressor. That is, it was known that the lubricating performance equivalent to the conventional CFC-12/mineral oil could not be obtained by the improvement of the ester base oil alone, and therefore the sliding part and additive were studied at the same time.

In the next step, the chemical stability of oil was evaluated. An ester oil is synthesized by reaction of acid and alcohol by removing water. This reaction is an equilibrium reaction, and the product is easily decomposed into the original acid and alcohol in the presence of water. Changes of total acid value depending on water content, temperature and time are shown in Fig. 3. Assuming only hydrolysis, the reaching point of total acid value by the decomposed acid may be easily calculated in the following equivalent formula.

$$AV = \frac{Y \times M_{KOH} \times 10^3}{M_{H_2O} \times 10^6}$$

where AV : total acid value [mgKOH/g]

Y : water content in oil [ppm]

M_{KHO}: molecular weight of potassium hydroxide

M_{H_2O}: molecular weight of water

Actually, however, since the reaction is an equilibrium reaction, an unreacted moisture remains, and the reaching point of the total acid value tends to be slightly lower than the calculated value. To the contrary, if elevation of total acid value due to acid produced by pyrolysis may be considered, the reaching point may be slightly higher than the value of the equivalent formula.

On the other hand, ester oil has such property so even in the refrigerating cycle incorporating a dryer, it is estimated that hydrolysis cannot be avoided in a long-term use because of the high equilibrium moisture content.

Accordingly, in order to neutralize the acid produced by hydrolysis as well as to remove moisture existing in such low moisture region, it was attempted to use epoxy additives conventionally known. The moisture removing effect by epoxy additives is shown in Table 2.

The difference of effect by the variety of additives was not clear, and in the presence of epoxy group, the total acid value does not elevate, and it is possible to remove moisture and neutralize the acid produced by hydrolysis.

Hitherto, the phenyl epoxy was used because of its high solubility in mineral oil, but it is hardly soluble in HFC-134a. Besides, the product produced by polymerization is not dissolved in oil refrigerant, and precipitates in condenser or capillary, and in a worst case it may cause capillary choke to induce refrigeration performance drop. Considering from these factors, in the case of HFC-134a, in selecting the epoxy additive, it was the first condition in choice that it should be dissolved in oil/refrigerant if polymerized.

An epoxy additive was equivalently mixed with water in the presence of a trace of HFC-134a, and was sufficiently polymerized to obtain a product of high viscosity. This product was mixed in a refrigerant, and the solubility was investigated in a range from ordinary temperature to low temperature. In particular, the fluidity in the low temperature region where the product was likely to stay in the piping was carefully evaluated. The relation between temperature and fluidity is shown in Fig. 4. Soluble additive A, as compared with phenyl epoxy which represents the conventional epoxy additives, is characterized by the fluidity of polymerization product. At low temperature, too, it was found to be dissolved in refrigerant and oil and not to cause floccing or similar phenomenon. Likewise, more reactive additive B having phenyl epoxy group lost its fluidity when polymerized, and hence it was found that the fluidity of the polymerization product is impeded in the presence of phenyl group.

2.2 Improvement of lubricity

To improve the lubricity, both the sliding part and the additive were studied.

Concerning the improvement of the sliding material, the plane-on-roller type of wear test machine was also used. In the existing materials, the lubricity on the sliding surface was effective for enhancing the extreme-pressure properties not only by the oil but also by the refrigerant, and therefore the reproduction test of abrasion and injury in refrigerant atmosphere was repeated, and the test condition was established, and characteristics of sliding materials were evaluated.

In selecting the sliding material, corrosion resistance was included in the criteria showing that hydrofluoric acid generated by decomposition of refrigerant of HFC-134a is more corrosive than the hydrochloric acid generated by the existing CFC-12, and also that the ester oil is likely to produce carboxylic acid by hydrolysis. Table 3 shows the results of lubricity test by plane-on-roller type of wear test machine and results of corrosion loss by hydrochloric acid and hydrofluoric acid by selecting characteristic materials from combinations of scores of types. There was a high correlation between the corrosion resistance evaluation result by hydrochloric acid and the abrasion amount, and a material of high corrosion resistance is found to be also resistant to abrasion. Besides, the nitriding treatment was considerably worsened by hydrofluoric acid, and the abrasion characteristic in the HFC-134a atmosphere was inferior, but since the corrosion resistance evaluation by hydrochloric acid was superior, it was considered that a favorable lubricity would be shown in the existing CFC-12.

In particular, the ceramic material of high corrosion resistance does not wear at all in the abrasion test result. When the opposite material is changed, the cobalt alloy steel present an abrasion resistance equivalent to that of ceramics. Hence, considering the material cost and ease of machining, not only ceramics but also cobalt alloy steel were selected as sliding part.

In order to further enhance the lubricating properties, the hitherto highly-reputed phosphorus compound additives, and fluoric compound or molybdenum containing organic additives were evaluated in abrasion test, and the efficacy of phosphorus compound additives was studies. (See Table 1.) In addition, by short-term confirmation test by simple unit at high temperature, generation of foreign matter was investigated, but nothing notable was generated.

In the material specification after these element improvements, the life test was conducted in refrigerator.

3. Results of life test

The life test in refrigerator is, unlike the simple unit test, conducted in the actual refrigerator conditions consisting of the cycle of compression, condensation, expansion and evaporation, with only the temperature conditions made severer. List test was conducted for three months, and conditions are given below.

	Temperature	Pressure
Evaporator	-15°C	-15°C saturated pressure
Condenser	60°C	60°C saturated pressure
Compressor	135°C	60°C saturated pressure

The test specification and results are shown in Table 4.

As far as seen from the temperature changes in the refrigerator compartment and inputs, marked lowering of refrigerating performance was not observed in any specification. Observing the oil deterioration, without additives, the total acid value was 0.09 mgKOH/g, and with epoxy additive, it was 0.01 mgKOH/g, achieving the target of 0.05 mgKOH/g or less. The abrasion with the conventional sliding parts was 200 μm (not shown), and by changing the material of the sliding part it was decreased to 43 μm, and when combined with the epoxy additive, it was less than 10 μm, and a nearly satisfactory result was obtained. However, in the refrigerator charged with phosphorus additives, the abrasion was slightly large, about 20 μm, and the total acid value was also higher. Furthermore, in the refrigerator, white foreign matter was formed in the dryer unit.

The result of analysis of the white foreign matter by XMA. is shown in Fig. 5. Comparing the main components of the white foreign matter with the peak of iron phosphate, since peaks of phosphorus and iron are nearly unchanged, it is highly possible to be iron phosphate, but part of organic matter is contained.

Iron phosphate is soluble in ester oil, but is hardly solube in refrigerant, and therefore it is estimated to precipitate in the portion where the refrigerant ratio is high in the liquid such as the condenser, but in the equipment for expansion by capillaries of small inside diameter as in refrigerator, possibility of inducing shortage of circulation of refrigerant due to choking with foreign matter is very high.

4. Discussion

Hence, estimating the cause of oil deterioration and abrasion of sliding part in the HFC-134a/ester oil, the carboxylic acid caused by hydrolysis reacts with the surface of sliding part to induce abrasion, and the active metal formed by abrasion acts catalytically to promote deterioration of oil. The product of oil deterioration reacts with the surface of sliding part to further encourage abrasion. The iron carboxylate formed at this time is a factor of coloring of oil.

That is, the mechanism for promoting oil deterioration and abrasion of the HFC-134a/ester oil is a chemical reaction, and to avoid this, it is desired to set up the refrigerating cycle eliminating moisture which is an initiator of reaction as much as possible, and also to set up a cycle of low temperature and low pressure in order to suppress chemical reaction.

The effect of phosphorus additives is noted, but is not so significant as that of epoxy additive. This is because the phosphorus additives itself hardly acts in the oil/refrigerant of high polarity, that is, the active surface metal cannot be coated sufficiently against the abrasion by chemical reaction.

Meanwhile, effects of impurities in refrigerant, effects of organic materials existing in the refrigerating cycle, and catalytic effects are now being investigated continuously.

5. Conclusions

As discussed herein, in order to apply the HFC-134a in the compressor of high internal shell pressure type that is likely to be influenced by lowering of lubricity of refrigerant, the ester oil should be selected in consideration of the oil return and electric insulating performance. To guarantee durability, by using a sliding part excellent in corrosion resistance, removing moisture by dryer, and using an epoxy additive, the oil deterioration may be inhibited. At the same time, by enhancing the corrosion resistance of the sliding surface, the rate of forming active metal surface is decreased, and abrasion may be prevented. By the combination of these points, the durability of the refrigerating cycle including the compressor may be assured for a long term.

Henceforth we are planning to study hydrogen fluorocarbons (HFC-32, HFC-125, etc.) that are also expected to be used as substitutes for chlorofluorocarbons in the same manner and concept in order to develop practical substitutes as soon as possible.

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3) A. Kawamoto and T.A. Kojima, "Expelimental Investigations in Domestic Refrigerator-Freezers with HFC-134a", CFC Issue and Greenhouse Effect, Conference Proceedings, p362-p371, May 1991.

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Table. 1 Lubricity of oils and additives

Refrigerant	CFC-12	HFC-134a			
Oil / Additives	Mineral	Ester			
		Hindered N	Complex N	Complex S	Carbonate M
None (base oil)	100 None	70 Yes	70 Yes	270 None	400 Yes
Phosphorus	——	160 None	200 Yes	270 None	270 Yes
Molybdenum	——	130 Yes	70 Yes	Seizure	——
Fluoric	——	400 Yes	Seizure	——	Seizure

Upper: abrasion (index)
Lower: scrach or adhension

Table. 2 Comparion of epoxy additives

Refrigerant	HFC-134a			
additive	Phenyl epoxy	Epoxy A	Epoxy B	None
TAN (mgKOH/g)	0.02	0.01	0.01	0.25
Reaction ratio	100%	100%	90%	——
Conditions	·Water content 100ppm ·Temperature 448K ·Test term 2weeks ·Refrigerant/Oil=1/1			

Table. 3 Lubricity and corrosion

Refrigerant		CFC-12	HFC-134a			
Vane		Steel			Treatment	Ceramics
		Current	Mo alloy	Co alloy	Nitriding	
Lubricity with opposite materials						
	Cast iron	100 None	270 None	70 Yes	Seizure	0 None
	Steel	430 Yes	830 Yes	70 None	600 Yes	70 None
Corrosion loss						
	HCl	100	147	33	32	1
	HF	754	576	384	631	10

Upper: abrasion (index)
Lower: scrach or adhension

Table. 4 Durability test results

Test specification						
Refrigerant		CFC-12	HFC-134a			
Oil		Mineral	Ester			
Additive	epoxy	None	Yes	None	Yes	
	phosphorus	None	None	Yes	None	
Test term			3 months			
Performance						
FC Temprature changes [K]		0.3	0.7	0.4	0.2	
PC Temprature changes [K]		0.1	0.5	1.0	0.9	
Input changes [Wh]		1	5	4	4	
Oil changes						
Color [ASTM]		L3.0	L2.0	L3.0	L2.0	
TAN [mgKOH/g]		0.01	0.01	0.05	0.09	
Water content [ppm]		17	9	33	22	
Foreign matter		None	None	Yes	None	
Vane wear						
Abrasion [μm]		7	8.5	20	43	
Surface roughness [Rz]		1.1	0.3	0.2	0.4	

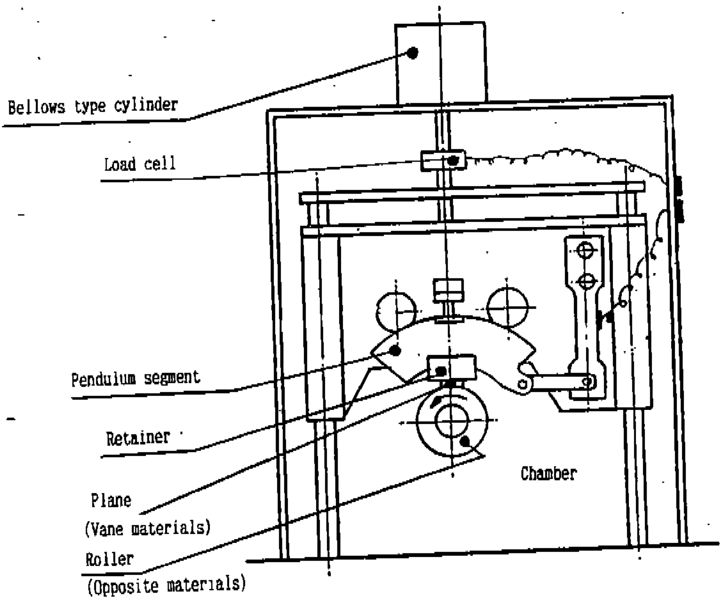


Fig. 1 Plane-on-roller type of wear test machine

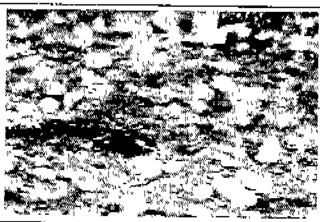
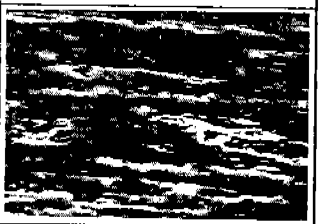
Refrigerant atmosphere	CFC-12	HFC-134a
Surface angle 0 × 800		
Inclined surface angle 60° × 2400		
Wear state	normal wear	scrach and adhension

Fig. 2 Metal surface of current material

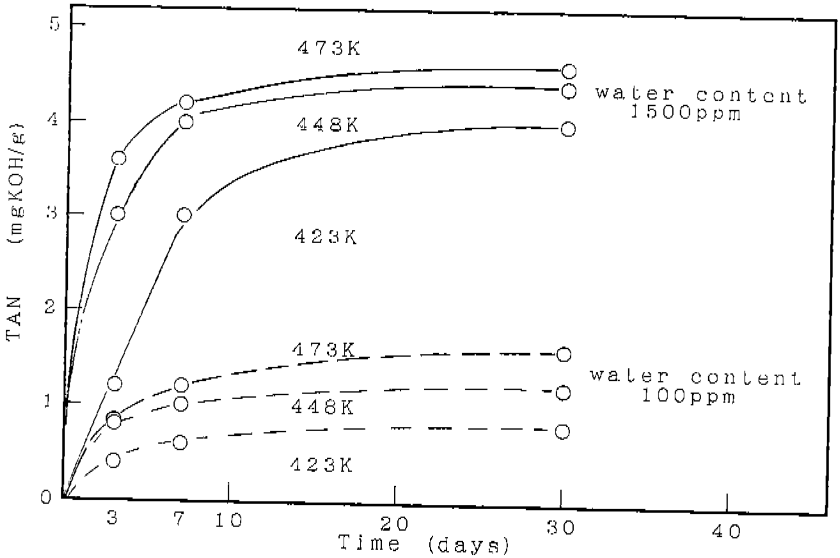


Fig. 3 Effect of water content

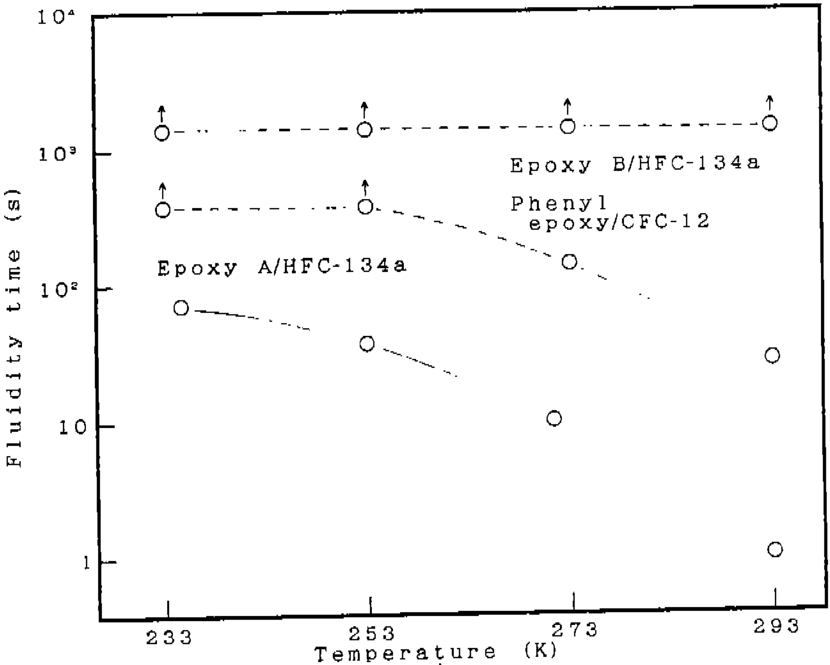


Fig. 4 Flow property of polymerized additives

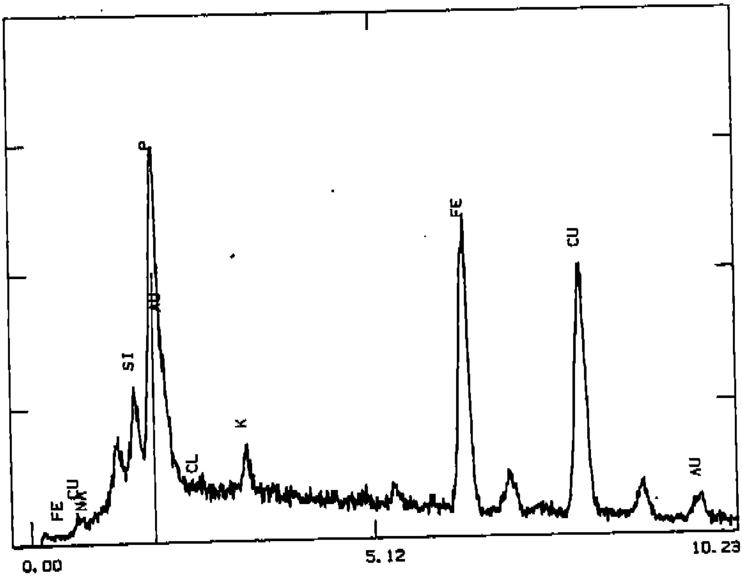


Fig. 5 XMA analysis of foreign matter