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Selection and Performance of Synthetic and Semi-Synthetic Lubricants for Use with Alternative Refrigerants in Refrigeration Applications

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TRIBOLOGICAL ANALYSIS OF METAL INTERFACE REACTIONS IN LUBRICANT OILS/CFC12 AND HFC134a SYSTEM

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ABSTRACT

A tribological study was made on the relationship between surface composition and wear of iron-based metals tested in candidate lubricants soluble with HFC134a. Emphasis was placed on the microscopic study and the X-ray photoelectron spectroscopic study on the surfaces of different material combinations including grey cast iron/steel tested in five lubricant/refrigerant mixtures including polyalkylene grycol (PAG)/HFC134a. Observations show the formation of iron oxides in PAG/HFC134a, while iron chloride in mineral oil/CFC12. The formation of solid lubricant films such as iron sulfide or phosphide compounds in the surface zone apparently improve lubrication properties between the surfaces eventually contributing to dramatic reduction of wear in a new lubricant/HFC134a.

INTRODUCTION

CFC12 has been widely used as the refrigerant circuits for household refrigerators. As a substitute for CFC12, HFC134a which contains no ozone-depleting chlorine is the leading candidate, because of its similarity to CFC12 in thermodynamic properties, chemical properties and compatibility with refrigerator systems. Problems in adopting HFC134a are that a compatible lubricant has not been found which assures trouble free operation over the expected life of the compressor.

Mineral oils have usually been used as lubricants in reciprocating compressors, but HFC134a has a poor solubility in mineral-based lubricating oils. And mineral oils, which contain cyclic compounds, might maintain adequate hydrodynamic film thickness. Polyglycol oil, a lubricant candidate for its solubility in HFC134a, may not maintain an adequate hydrodynamic film under reciprocal or rotational motion because it consists of a chain compound structure.

CFC12 is known to make a significant contribution to lubrication in compressors due to the presence of chlorine atoms (1)(2)(3). Since HFC134a contains no chlorine, it is not clear if this added lubricity effect will be seen with a new lubricant/HFC134a mixture. As a results, some improvements in a lubricant or oil additives may be required if the long reliability of present system is to be maintained. There have been intensive works for a new lubricant that is soluble in HFC134a and that meets refrigerant lubricant requirements such as lubricity and excellent stability. A large number of candidates are available for evaluation.

Our primary concern is with selecting a new lubricant which requires minor modifications in compressor design. In this regards, compatibility of iron-based metal used in the current compressors with new lubricants/HFC134a has been evaluated

In this investigation, a special emphasis is placed on the results of wear tests and the X-ray photoelectron spectroscopic (XPS) study. The XPS has been employed previously to characterize the surface species on steel surfaces after wear testing (4).

On the basis of the wear tests and the XPS study, a tribochemical consideration has been made on the effects of PAG, other lubricants such as ester-type synthetic oil, and antiwear additives. A metallurgical consideration based on the microscopic study has provided us basic information on the effects of hardness, grain size and the shape of graphite.

EXPERIMENTAL PROCEDURE AND APPARATUS

Falex Test

The bench test apparatus used was a standard Falex Lubricant Tester (Faville-Le Vally Corp.). The schematic diagram (Fig.1) shows the tester and the test assembly (1). The tester operates at a constant speed of 290rpm. The V-block-pin design is self-aligning. As is shown in Fig.1, we modified the method of attaching the pin from the original brass locking pin to a bolt. This modification was required to minimize the errors in the measurements due to deformation of the brass locking pin. The material and hardness of the V-blocks and the pins are listed in Table 1.

Table 1- The material and hardness of Falex test pieces

		material	hardness(Hv)
pin	No.1	grey cast iron	278
	No.2	nodular cast iron	335
	No.3	chromium molybdenum steel	919
V-block	No.1	steel	306
	No.2	grey cast iron	374
	No.3	sintered alloy	-

Prior to each test run, the pin and the V-blocks are cleaned thoroughly in toluene, a nonpolarizing solvent. The cleaned test pin and V-blocks are weighed accurately prior to assembly into the test machine. After assembling the test system, gaseous refrigerant is bubbled through the test lubricant for at least 15 minutes. It is introduced into the system through a tube placed at the bottom of the oil pan as close to the test pin as possible. The lubricant, pin, and V-blocks are heated to 80 °C during break-in and the temperature is controlled within ±3 °C during the whole test. The tester is then started and loaded to 200lbs (91kg). The system is operated at 200lbs for 5 minutes after which the load is increased to 300lbs (136kg). The ratchet wheel pressure loader is advanced to maintain constant load throughout the course of the test. Refrigerant is bubbled continually during the test at a rate of approximately 12 liters/hr.

The test terminates after running for 30 minutes. The pin and V-blocks are carefully removed from the system upon termination of the test. They are thoroughly cleaned in acetone, a polarizing solvent, either to remove lubricant and loose wear residues. The cleaned and dried pin and V-blocks are then reweighed accurately and the weight difference between the new and the used test piece is recorded as wear in milligrams.

X-ray Photoelectron Spectroscopy

XPS is useful for in-depth monitoring of the binding energy (Eb) of each element. The energy levels tend to shift during compound formation, and these shifts indicate changes in the chemical state of the components

The XPS spectra were recorded with a Shimadzu ESCA-850M spectrometer with Mg Kα radiation (1253.6 eV) as the X-ray source. A schematic of the apparatus is shown in Fig.2. The base pressure in the analyzer chamber was better than 5×10^{-6} Pa during analysis. Argon ion sputtering was performed at 4×10^{-4} Pa with beam voltages of 2 kV and sample currents of 20 μA/cm^2. The sample was rotated during sputtering in order to etch the sample uniformly. The values of electron binding energy, drifting due to a surface charging effect, were calibrated by the use of C1s reference. Data collection and subsequent analysis were accomplished with a computer system using DEC (JAPAN Digital Equipment Company) software. The software package included essential subroutines for data analysis such as smoothing, deconvolution and curve fitting. After wear-testing, a test pin which has been cut to 5x5mm^2 is cleaned in acetone. It is then put into the chamber immediately. Measurements begin when the base pressure in the analyzer chamber reaches better than $5X10^{-6}$ Pa.

Lubricants and Additives

The physical properties of the lubricants used in the study are given in Table 2.

Table 2- Physical properties of the lubricants

oil	compound	kinematic viscosity(cSt) at 40°C	at 100°C	viscosity index	water (ppm)
A:	polyalkylene glycol(PAG)	24.3	5.0	136	350
B:	PAG+antiwear additive	25.2	5.1	138	352
C:	ester-type synthetic oil	30.7	5.2	94	75
D:	perfluoropolyether	27.0	6.0	150	0
E:	mineral oil	15.4	3.4	87	30

Oil A is a polyalkylene glycol (PAG) without antiwear additive, Oil B is a polyalkylene glycol containing antiwear additives (phosphide), Oil C is an ester-type synthetic oil containing antiwear additives (phosphide), and Oil D is a perfluoropolyether. Oils A, B, C and D are synthetic refrigeration compressor lubricants recently developed to have mutual solubility with HFC134a. Oil E is a parafin mineral oil already used in reciprocating compressors. During the experiments, water content must be controlled because PAG has full water solubility. PAG can be dehydrated by heating to 80°C and by bubbled with dried gaseous nitrogen. Solubility is measured by coulometric analysis of water titration, the method due to Karl Fischer.

RESULTS AND DISCUSSIONS

Wear Test Results

The Falex tests were carried out in a variety of lubricant and refrigerant mixtures. As shown in Table 2, a total of five lubricants, including the conventional mineral oil, were used. Five materials including steel and grey cast iron were selected. Five combinations of the materials, including grey cast iron/steel and nodular cast iron/grey cast iron combinations, were tested in the lubricants saturated with refrigerants. The material combinations were selected on the basis of their potential for requiring minimum changes in compressor design.

The sums of pin and V-blocks wear tested in four lubricants are depicted in Fig.3. As shown in Fig.3, a significant amount of wear occurs in PAG/HFC134a. Strong polar radicals such as -OH present in PAG could form a stable film on the metal surface. The stable film formation, together with the higher viscosity and the higher viscosity index shown in Table 2, fails to account for the poor lubricity of PAG. Thus we do not have a mechanism to explain the significant amount of wear in PAG, except to suggest that it has to do with the FeO and FeOOH formation on the surface, detected by means of the XPS study which will be detailed in the following section.

Oil B which contains a phosphoric additive in PAG exhibits better lubrication qualities than PAG. The lubrication properties of Oil C/HFC134a are approximately equivalent to those of Oil E/CFC12.

Possible accounts for the better lubricity of ester-type synthetic oil/HFC134a and mineral oil/CFC12 are the presence of phosphide compounds and iron chloride in the surface zone of the tested samples respectively. It can be seen from Fig.3 and Table 2 that the amounts of wear roughly depend upon water content in the lubricants. This dependency suggests that water quantity dissolved in a lubricant has a detrimental effect on lubrication properties in HFC134a.

It would be in order to consider that the wear amounts of the test pieces depend upon their surface qualities such as hardness and roughness which vary with small differences in their composition, fabrication or treatment. For the purpose of examining the effects of the differences, we have tested three groups of test pieces of the same materials with different hardness given in Table 3.

Table 3- The vickers hardness (Hv) and wear of Falex test pieces

	pin grey cast iron	V-block steel	wear in mg
Lot 1	278	306	58.5
Lot 2	263	288	2.9
Lot 3	278	236	1.7

The pins are of grey cast iron and the V-blocks of steel. In spite of using the same materials, differences can be seen among the wear in three different lots as shown in Fig.4. The figure also shows that the amounts of wear apparently decrease as the hardness of V-blocks decreases. There is, however, no straightforward relationship between the hardness and the degree to which the wear occurs. We have made observations on the arrangement of crystals in the vicinity of test piece surface by means of the microscope.

Fig.5 is a microscopic view of the cross-sectional crystal structure of the V-blocks after completion of the test run. The picture of Lot 1, with the maximum wear, clearly shows the elongation of crystal grains due to residual stress caused by its manufacturing process. This tendency is also seen in Lot 2, but the crystal strain is less than that in Lot 1. In the case of Lot 3, with the minimum wear, the crystal grain is isotropic and large. In the case of crystal structure with the residual stress like Lot 1, the bonding between the crystal grains seems to become weaker as the strain is released by temperature rise. Then minute particles are supposed to be torn off the metal surface, which results in a significant increase in wear. The wear occured in the surface with such crystal structure is accelerated in PAG since its poor lubricity increases the surface temperature due to frictional heating. Therefore, in order to minimize the wear of metal surface lubricated with PAG, the material is needed to be properly treated for rearrangement of its crystal structure.

In view of the critical influence of surface treatment on improved lubrication in PAG/HFC134a, we have extended our works to study the effects of surface coating and oil additives in the lubricants/HFC134a. Previous works have shown that sulfide has a chemical stability against water (5) and iron sulfide coatings form an effective boundary lubricant film (6). On the basis of the good lubrication property of sulfide, the pins of grey cast iron coated with iron sulfide have been tested in the lubricant/HFC134a on the Falex lubricant tester. The pins and the V-blocks have been selected from Lot 1 samples whose surface zone are pre-stressed in the manufacturing process. In the test runs, PAG and PAG blended with zinc dialkyldithiophosphate additive (ZDTP) have been employed. The concentration of ZDTP is 1 wt%.

Fig.6 indicates that the additive has provided a dramatic reduction of wear, more than 85% reduction of the wear which occured in PAG/HFC134a. The total amounts of wear occured in the samples with iron sulfide coating are no more than one third of the ones without coating as shown in Fig.6. The relatively small contribution to wear reduction of the coating may come from failing to make a proper control of the surface roughness. As shown in following, the formation of a solid lubricant such as iron sulfide can account for the reduction of wear achieved by adding ZDTP and by coating with iron sulfide.

In the preceding sections, discussions have been primarily made on the results of the test run conducted with the grey cast iron/steel combination. Fig.7 presents the amounts of wear volume measured on all the material combinations listed in Table 1. The figure indicates that the combination of nodular cast iron/grey cast iron exhibits the least wear volume among the material combinations tested in PAG/HFC134a. The wear is comparable to the wear volume occured in the conventional mineral oil/CFC12. The same thing has been observed in the other new lubricants, such as Oils B, C, and D in HFC134a.

Since graphite particles are spherical, in addition to the improved mechanical properties, each graphite particle is bigger and more isotropic than flake graphite, so the maintenance of the hydrodynamic film thickness of PAG is supposed to be improved. The cross-sectional observations of nodular cast iron after wear testing are shown in Fig.8. Clearly the amount of graphite particles of nodular cast iron is greater than in the case of grey cast iron at the metal surface.

XPS Analysis

We have employed the X-ray photoelectron spectroscopic study to see what happened to the samples working in the lubricant/refrigerant mixtures. We took the same sample that had been tested on the Falex tester and put it on the spectrometer to examine for chemical compounds in its surface zone.

Curves shown in Fig.9(a) are typical photoelectron spectra for the pin with the minimum wear occured in mineral oil/CFC12. The five curves shown in Fig.9(a) are different Fe2p spectra obtained at the different depths from the surface. The curve 1 is the spectrum from the surface, the outermost layer, and the curve 2 is the spectrum from the layer approximately 100A below the surface. Peaks in the vicinity of Eb=711 eV indicate the presence of iron-based compounds including iron chloride FeCl3. Similarity in the forms of the curve 1 through 5 shows that chemical composition is uniform in the vicinity of the surface from the surface down to the layer approximately 400A below the surface.

The five curves shown in Fig.9(b) are different Cl2p spectra observed at different layers from the surface. Peaks found around Eb=199 eV are the positive indications of chlorine-based compounds including FeCl3. It can be easily seen from Fig.9(a) and Fig.9(b) that iron chloride is formed in the surface zone of the sample tested in the presence of CFC12. Good lubricity of iron chloride can account for the wear data obtained on the Falex tester in the presence of mineral oil/CFC12.

Fig.10 shows photoelectron spectra for the compressor piston which has run for 1400 hours in the commercial refrigerator-freezer designed for CFC12 and mineral oil. We see small differences in some of the ten curves, but in the basic outline they look very much alike. Peaks in the curves shown in Fig 10(a) as well as Fig.10(b) indicate that iron chloride is formed in the surface zone down to 900A below the surface of the piston in the presence of CFC12. Fig.9 and Fig.10 indicate that iron chloride formation takes place in the compressor piston as well as the test pieces on the Falex tester. It is interesting to note that significant amount of iron chloride is formed in the Falex test run although it can not be continued for satisfactorily long period of time. Good agreement between the results of the two experimental runs enables us to employ the Falex test as a useful means for selecting proper materials for a given lubricant/refrigerant mixture.

Photoelectron spectrum for the pin tested in PAG/HFC134a is shown in a somewhat different form in Fig.11. From the peak dissolving analysis, the metallic iron component is slightly seen at the virgin surface created by shearing force. The major component of the peak is iron oxide FeO, so it is thought that the main reaction at the interface is oxidation in the presence of PAG/HFC134a. In addition, Fig.11 indicates the presence of FeOOH produced in a possible iron-water reaction, and FeF_3 produced in iron-HFC134a reaction. Thus, the surface worked in PAG/HFC134a shows no evidence of a solid lubricant such as iron chloride. This may lead to serious compressor lubrication problems. The remarkable amounts of wear in the presence of PAG/HFC134a stated in the preceding section can be reasoned by lack of the self-lubricant substance on the surface.

Curves shown in Fig.12(a) and Fig.12(b) are photoelectron spectra for the pins tested in ester-type synthetic oil/HFC134a and in perfluoropolyether/HFC134a respectively. Peaks in the curves in Fig.12(a) indicate that phosphorous component P^{3+} exists in the surface zone. Close inspection of the curves shows the gradual decrease in peak height in the curves, which suggests the quantity of P^{3+} decreases as the depth increases. The effect of phosphorus on lubrication properties has been hypothesized as follows. First, iron phosphide is formed on the convex spots in the surface by local heating. The iron phosphide reacts with iron to form an alloy with a low melting point (less than 500℃). The alloy melts and flows to fill concave spots in the surface, which results in flattening the worn surface. Thus, pressure reduction caused by the increase in the area of contact between two surfaces leads to less metal-metal contact due to less frictional heating at the interface (5). In Fig.12(b), the peak which appears in the curve 1 at Eb=669 eV and disappears in the curve 3 indicates a radical derived from the lubricant. We believe this is the evidence of lubricant contamination. Peaks which appears in the curve 2 through in the curve 9 at Eb=690 eV shows the existence of iron fluoride.

Curves shown in Fig.13(a), (b) and (c) are photoelectron spectra for the pins tested in PAG containing ZDTP additive/HFC134a. Similarity in the forms of the curve 2 through 10 in Fig.13(a) shows uniform composition in the vicinity of the surface. Peaks found at Eb=162 eV indicate the presence of sulfide including iron sulfide. Curves in Fig.13(b) are in somewhat complicated forms. A few peaks are observed in the curves. The peaks at Eb=139 and 134 eV indicate $-PO_4$ and P^{3+} respectively. The intensity of P^{3+} component in PAG containing ZDTP/HFC134a is smaller than that in ester-type oil/HFC134a with smaller wear as shown in Fig.12(a). A comparison Fig.3 with Fig.6 indicates that the wear occured in ester-type oil/HFC134a is approximately one third of that in PAG containing ZDTP/HFC134a. Thus, P^{3+} component is supposed to have a primary effect on lubrication properties. Curves in Fig.13(c) indicates the existence of zinc sulfide. Since these compounds such as phosphide, iron sulfide and zinc sulfide have the property of solid lubricant or prevent metal-metal contact, the ZDTP additive can be useful in improving the lubricity of PAG/HFC134a.

CONCLUSIONS

Wear tests and X-ray photoelectron spectroscopic study were made on iron-based materials in new lubricants saturated with HFC134a. Based on the data, the following conclusions are drawn on relationship between surface composition and wear of surface tested.

1)In mineral oil/CFC12, XPS analysis shows that iron chloride $FeCl_3$, which has solid lubricant properties, is formed at the metal surface both in Falex tests and in refrigerator-freezer tests.

2)Amounts of wear occured in polyalkylene glycol/HFC134a mixture are approximately twenty times larger than those in mineral oil/CFC12. The oxidation of iron primarily occurs in the surface zone in the presence of polyalkylene glycol/HFC134a, which results in the formation of FeOOH and FeO that could account for the significant wear.

3)The wear depends upon the microstructure in the suface zone, such as the shape of grains, and water dissolved in a lubricant. Dramatic reduction of wear could be achieved by a proper surface treatment, such as heat treatment or coating with iron sulfide. The use of nodular cast iron/grey cast iron combination would provide improved lubrication performance.

4)The formation of phosphorous compounds and iron sulfide are observed in the surface zone by mixing PAG with phosphide and sulfide antiwear additive, respectively. The function of these solid lubricant could account for the wear reduction achieved by the PAG blended with antiwear additives.

The preceding conclusions and recommendations apply only to the iron-based materials. In addition, the conclusions are based upon the tests conducted with limited combinations of materials. Further investigation should be needed before it can be determined which lubricant is the best for HFC134a to be used in refrigerator-freezers. More specifically the work required are:

1)improvement in mutual solubility and lubricity over the entire range of temperature and pressure

2)accelerated life tests for compressors and product testing of refrigerator-freezers.

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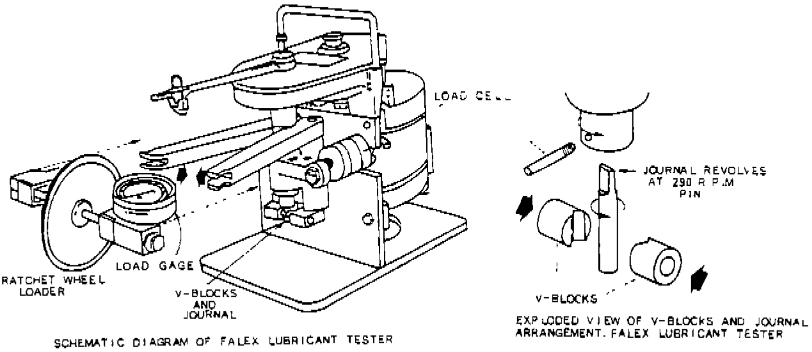


SCHEMATIC DIAGRAM OF FALEX LUBRICANT TESTER

EXPLODED VIEW OF V-BLOCKS AND JOURNAL ARRANGEMENT. FALEX LUBRICANT TESTER

Fig.1 — Schematic diagrams of Falex Lubricant Tester

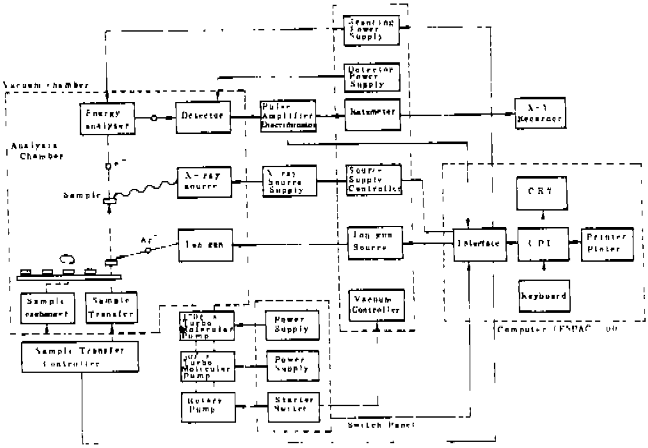


Fig.2 — Block diagrams of ESCA-850 spectrometer

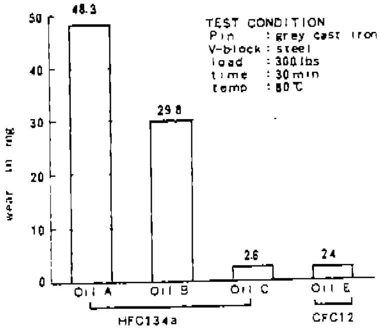


Fig 3 — The sum of pin and V-blocks wear for a variety of lubricants

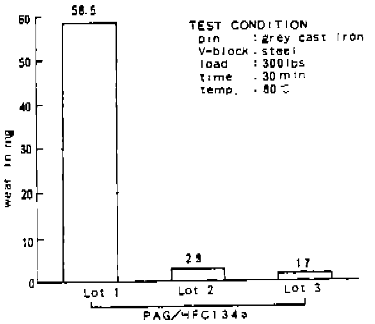


Fig.4 — The difference in wear between three different lots in PAG/HFC134a

Lot 1 Lot 2 Lo.t 3

Fig.5 —The cross-sectional crystal structure observed for the V-blocks after completion of the wear test

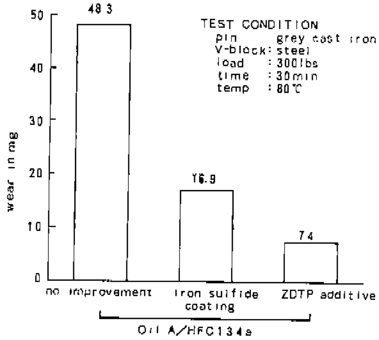


Fig.6 — Comparison of the effect on the surface treatment and oil additive with no improvement in Oil A/HFC134a

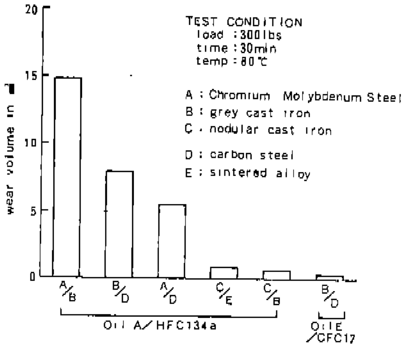


Fig.7 —The correlation between material combinations and amount of wear volume

nodular cast iron grey cast iron

Fig.8 —The cross-setional observations of nodular cast iron and grey cast iron after wear-testing

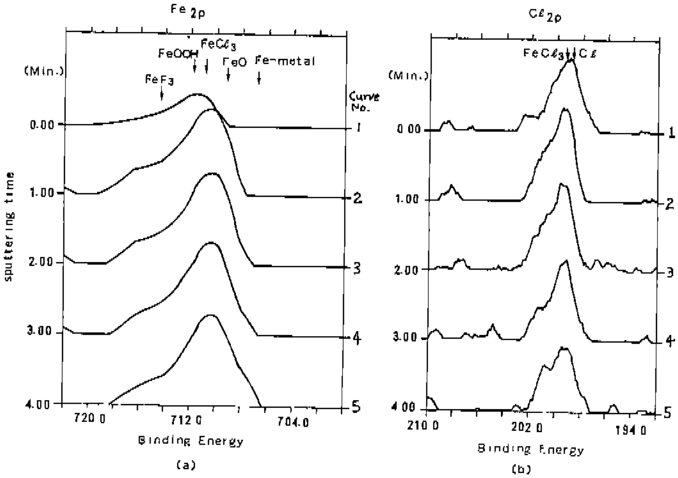


Fig.9 — Variations in Fe_{2p}(a) and $C\ell_{2p}$(b) photoelectron spectra for the Falex pin in Oil E/CFC12

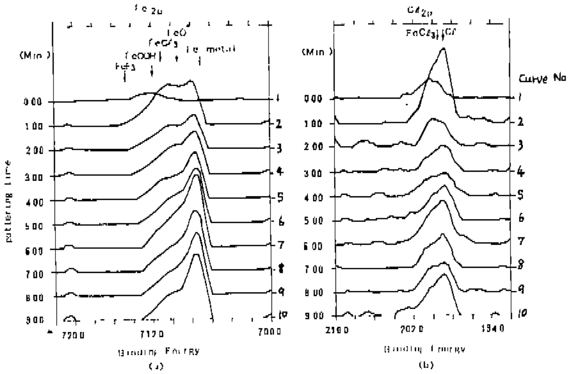
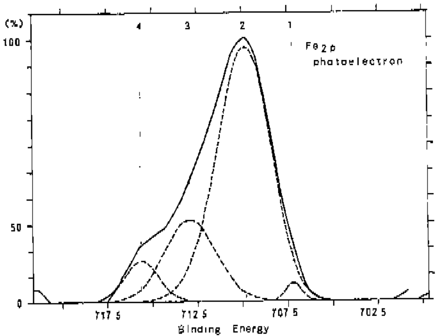


Fig. 10 — Variations in Fe_{2p} (a) and Cl_{2p} (b) photoelectron spectra for the piston surface in Oil E/CFC12 after refrigerator-freezer testing (1400hr)



No.	1	2	3	4
Name	Fe-metal	Fe O	Fe OOH	Fe F3
Peak Position(ev)	707.2	709.8	712.8	715.8
Area (%)	1.4	69.5	21.9	7.2

Fig. 11 —The resolved Fe_{2p} peaks observed after wear-testing in Oil A/HFC134a

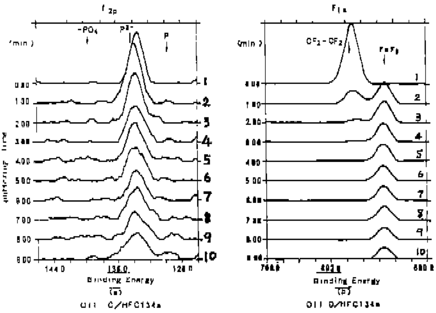


Fig. 12 —Variations in P_{2p} (a) and F_{1s} (b) photoelectron spectra after wear-testing

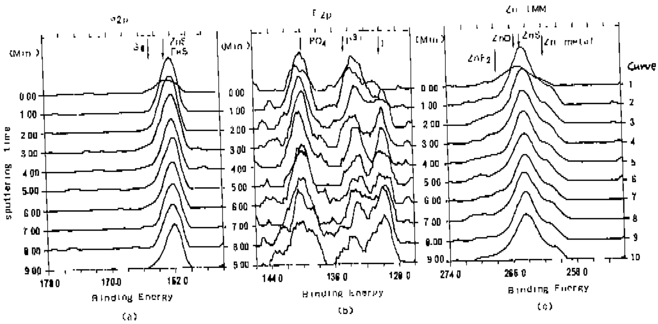


Fig. 13 — Variations in S_{2p} (a), P_{2p} (b) photoelectron and Zn LMM (c) Auger electron spectra in Oil A containing ZDTP/HFC134a after wear-testing