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THE EFFECTS OF TRIBO-CONDITIONS AND ANTIWEAR ADDITIVES ON THE DEGRADATION OF AN ESTER OIL AND ANALYSES OF DEGRADATION PRODUCTS

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ABSTRACT

The effects of tribo-conditions and antiwear additives on the degradation of an ester oil in refrigerant have been experimentally evaluated and the degradation products were analyzed. We have used hand-made pin and V-block apparatus in order to control temperature, load, rotating speed, and environmental gas.The degree of degradation of the ester oil was determined by the amount of sludge on the friction surface. Chemical analyses of sludge were performed by using pyrolysis gas chromatograph-mass spectrometry and thermogravimetry. It was found that the amount of sludge increases as the amount of antiwear additives increases under the lower load (10 kgf), and has a minimum in the addition range 0 to 2.5% of antiwear additives under the higher load (20 and 30 kgf). This result indicates that the antiwear film reduces the amount of the degradation products of the ester oil and inorganic products under the higher load. The amount of sludge increases as rotating speed and oil temperature increase. These results suggest that the surface temperature of contact and frictional resistance increase as the rotating speed and the oil temperature respectively increase.

INTRODUCTION

The various factors such as tribo-conditions, fresh surface of metal, exoelectron, kinds of base oil and additives, environmental gas, and oil temperature have influence on the degradation of lubricants on friction surface. It has been considered that the refrigeration oil is degraded on friction surface in the compressor for refrigerators and air-conditioners by these factors. It is very important to evaluate the amount of degradation products (sludge) of refrigeration oil from the viewpoint of the long-term reliability of refrigerators and air-conditioners because the cycle-pass of refrigerant are chocked with sludge.

There have been many investigations of the degradation of lubricants ; reaction rate[1], reaction mechanism[2], heat stability[3],analyses of oxidation products[4],[5]. However, the degradation of lubricants in these investigations was regarded as static chemical reaction, and there have been only a few investigations [6],[7] of dynamic(mechano-chemical) degradation on friction surface. In addition, there are no investigation that the degree of the degradation of lubricants is determined by the amount of sludge.

This investigation was carried out to evaluate the effects of tribo-conditions and antiwear additives on the degradation of an ester oil in refrigerant. The degradation of an ester oil was also considered by the analyses of sludge and friction surface.

EXPERIMENTAL DETAILS

Materials and test condition

Table 1 shows the properties of the ester oil. The additives are an antioxidant, a water and acid captor, and antiwear additives. The antioxidant is butyl hydroxy toluen. The water and acid captor is cyclohexene type compound. The antiwear additives are phenyl sulfur-phosphate type compound(Atype) and alkylphenyl phosphate type compound (Btype). The refrigerant is HFC 134a. We have used hand-made pin and V-block apparatus [8], shown in Fig.1, to evaluate the effects of tribo-conditions and antiwear additives on the degradation of the ester oil. The rotating pin is MoNiCr (cast iron) and V-block is SKH51 (steel, nitrided). The test specimen and conditions are summarized in Table 2.

Measurement of the amount of sludge

The ester oil after a test was diluted 3:1 with ethanol, and sludge was separated by filtering the diluted ester oil through a 0.45 μm PTFE membrane filter. The apparatus, the pin, and the V-block were washed with ethanol to remove the sludge adhered to them, and the washing was filtered. The amount of sludge was weighed on the microbalance.

Methods of analysis

Chemical analyses of sludge were performed by using pyrolysis gas chromatograph - mass spectrometry (py-GC/MS). Sludge in a quartz tube was weighed, and vaporized by using coilfilament type pyrolysis apparatus. The vaporized sludge was separated and analyzed qualitatively and quantitatively by using GC/MS. The organic proportion of sludge was measured by using thermogravimetry (TG). Table 3 and 4 show the analysis conditions of the py-GC/MS and TG.

Chemical analyses of the pin after a test were performed by using an electron probe micro analyzer (EPMA). The amount of the wear on the pin was obtained by measuring the width of the wear scar with a surface profilometer. Additional information on the nature of wear was obtained with a scanning electron microscope(SEM).

RESULTS AND DISCUSSIONS

Chemical analysis of sludge

The py-GC/MS chromatogram of sludge is shown in Fig. 2. The test conditions were ; 175°C, 30kgf load, 480rpm, 0.5% antiwear additives(A type and B type, respectively). The peaks 1, 5, and 6 were fatty acids. This result indicates that these peaks correspond to the degradation products of the ester oil. The peaks 3, 7 were phenol and alkylphenol,respectively. This result indicates that these peaks correspond to the degradation products of the antiwear additives. The peaks 2, 4 were carboaldehydecyclohexene and methylcarboaldehydecyclohexene, respectively. This result indicates that these peaks correspond to the degradation products of the water and acid captor. The other peaks were such compounds as hydrocarbons. It is found that the organic components of sludge consist of the degradation products of the ester base oil, antiwear additives, and water and acid captor.

Effect of the antiwear additives on the amount of sludge under the lower load(10kgf)

Fig.3 shows the relationship between the amount of sludge, the pin wear depth and the amount of the antiwear additives. The test conditions were ; 175°C, 480rpm. The 0.5% addition of antiwear additives of both A type and B type decreased the pin wear depth, and did not decrease the degradation products of water and acid captor, ester oil, and inorganic product. As a result, the total amount of sludge, including the degradation product of the antiwear additives, increased. These results indicate that the antiwear film reduces the real area of contact between rotating pin and V-block.

The addition above 0.5% of antiwear additives increased both the pin wear depth and the amount of sludge. It is also found that the degradation product of the antiwear additives was greatly increased in these cases. These results suggest that frictional resistance again increases as the amount of the antiwear film increases on addition above 0.5% of antiwear additives. The results described above agree with the finding[9] that frictional resistance have a minimum for an amount of surface film.

Effect of the antiwear additives on the amount of sludge under the higher load(20 and 30kgf)

The pin wear depth and the amount of sludge increased as load increased. This result indicates that the real area of contact and the temperature of the frictional surface increase as load increases.

The 0.5% addition of antiwear additives decreased both the pin wear depth and the amount of sludge. It is also found that the 0.5% addition of antiwear additives decreased the degradation products of the ester base oil and inorganic products, compared with no addition. These results indicate that the antiwear film reduces the real area of contact and the temperature of frictional surface.

The addition above 0.5% of antiwear addition increased both the pin wear depth and the amount of sludge. It is thought that this reason is similar to that described above.

Analyses of the pin

1. Surface topography

Topography of the wear scar produced on the pin was examined by using SEM. Fig.4 shows the SEM micrographs indicating the difference of the wear scar on the addition of antiwear additives. The test conditions were ; 30kgf load, 175°C, and 480rpm. The pin surface on addition of antiwear additives are comparatively smoother than that without antiwear additives. It is confirmed that the addition of the antiwear additive reduces the wear scar.

2. Surface chemistry

EPMA mapping study of the pins after a test was carried out to examine the amount of the antiwear film. Fig.5 shows the EPMA mapping of rotating pins. The test conditions were ; 30kgf, 175°C, and 480rpm. The amount of phosphorus on the worn surface of the pin on 5.0% addition of antiwear additive (B type) is 1.5 times as much as that on 0.5% addition of antiwear additive (B type). This shows that the amount of the antiwear film on 5.0% addition of antiwear additive is more than that on 0.5% addition of antiwear additive.

Effects of oil temperature and rotating speed on the amount of sludge

Fig.6 shows the effect of oil temperature on the amount of sludge. The test conditions were; 10kgf load, 480 rpm, and A type 0.5%, B type 5.0% antiwear additives. The pin wear depth and the amount of sludge increased as oil temperature increased. It is also found that the degradation products of the antiwear additives increase as oil temperature increases. These results suggest that frictional resistance increases as oil temperature increases when the antiwear film is enough to reduce the wear.

Fig.7 shows the effect of the rotating speed on the amount of sludge. The test conditions were ; 10kgf load, 175°C, and A type 0.5%, B type 5.0% antiwear additives. The pin wear depth and the amount of sludge increased as the rotating speed increased. It is also found that all components of sludge increases as the rotating speed increases. These results indicate that the temperature of frictional surface increase as the rotating speed increases.

CONCLUSIONS

The following conclusions were derived from the results and discussions.

1. The pin wear depth was minimized in the addition range 0 to 2.5% of antiwear additives.
2. The amount of sludge increased as the amount of antiwear additives increased under the 10kgf load. The amount of sludge was minimized in the addition range 0 to 2.5% of antiwear additives under the 20 and 30kgf load.
3. The pin wear depth and the amount of sludge increased as oil temperature and rotating speed increased.

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Table 1 Properties of ester oil

Color(ASTM)	L0.5
Viscosity(cSt)	56
Density(15°C, g/cm³)	0.98
Tan(mgKOH/g)	0.01
Solubility(R134a, °C)	
U-CST	>80
L-CST	− 27

Table 2 Test specimen and conditions

Ester oil(ml)	350
Additive(mass%)	
antioxidant	0.2
water・acid captor	0.5
antiwear(A)	0～0.5
antiwear(B)	0～5.0
R134a(g)	150
Load(kgf)	10～20
Temperature(°C)	60～175
Rotating speed(rmp)	120～960
Time(hr)	72

Table 3 Pyrolysis-GC/MS conditions

Pyrolysis apparatus	
Temperature(°C)	700
Time(s)	10
Amount of sample(μg)	300
GC/MS	
Initial temperature(°C)	40
Final temperature(°C)	280
Heating rate(°C/min)	10
Injection temperature(°C)	250
Column	HP5*
Acceleration voltage	70eV

* id0.25mm X 30m

Table 4 TG conditions

Initial temperature(°C)	25
Final temperature(°C)	600
Heating rate(°C/min)	20

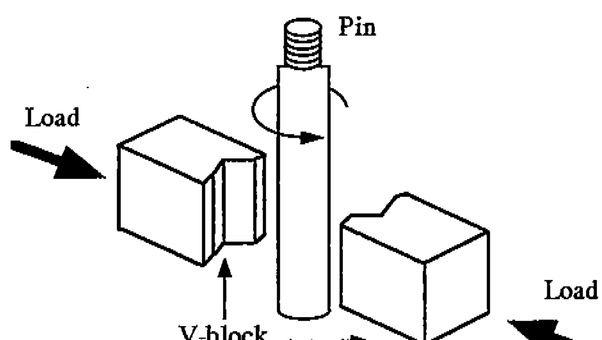


Fig.1 Hand- made pin and V-block apparatus

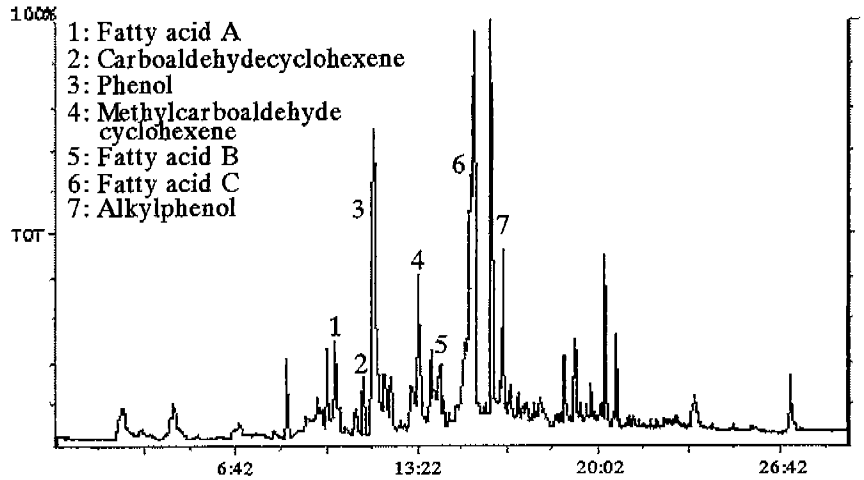


Fig.2 Py-GC/MS chromatogram of sludge

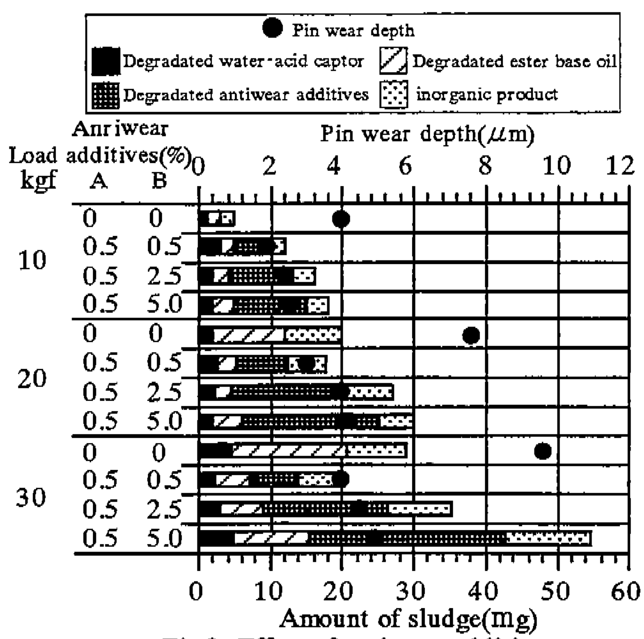
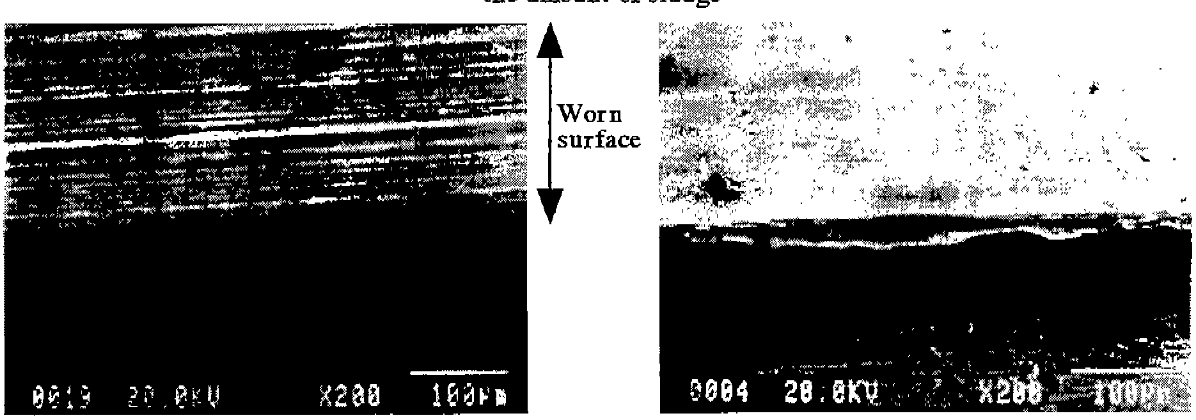


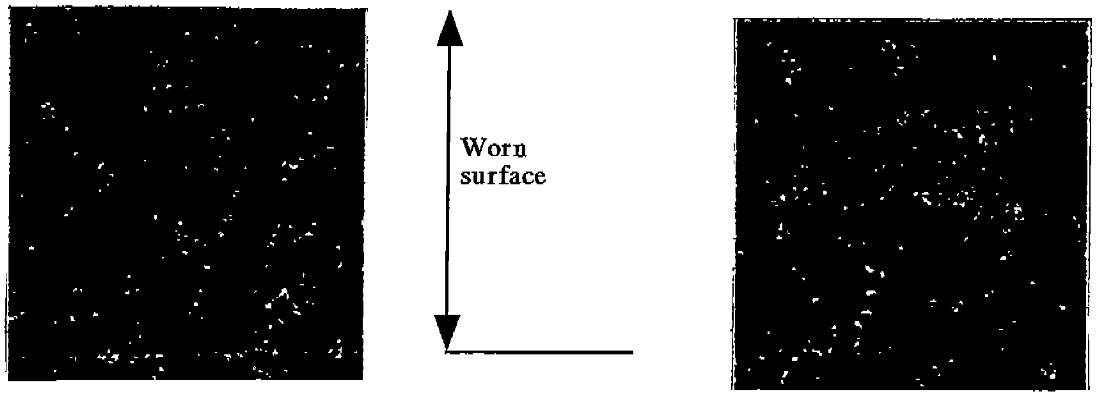
Fig.3 Effect of antiwear additives on the amount of sludge



(a) Antiwear additives A0%, B0%

(b) Antiwear additives A0.5%, B5.0%

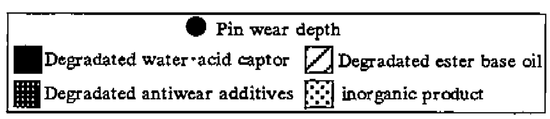
Fig.4 SEM micrograph of rotating pins



(a) Antiwear additives A0.5%, B0.5%

(b) Antiwear additives A0.5%, B5.0%

Fig.5 EPMA mapping of rotating pins



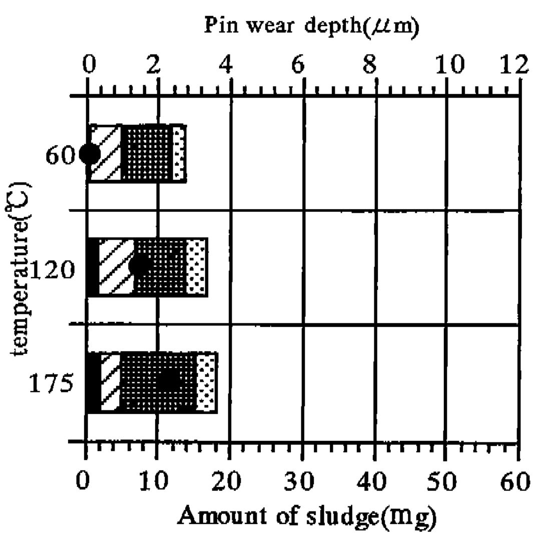


Fig.6 Effect of oil temperature on the amount of sludge

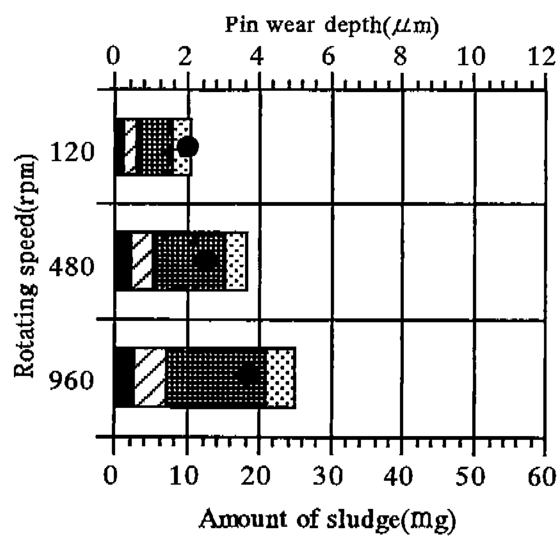


Fig.7 Effect of rotating speed on the amount of sludge