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Wear Scar Evolution during Four-ball Test in PAG Oil Containing Different Additives under R134a Refrigerant Environment

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Keywords： Four-Ball test; EP Performance; EP additives; AW additives

ABSTRACT

In this work, the extreme pressure performance of different additives blended with PAG oil was evaluated in refrigerant environment, and the wear scar evolution of four ball test was also monitoring step by step. The four-ball sliding wear test condition was set to simulate the operation of the components in the air conditioner compressor. The experiment results showed that the wear scar at the initial stage of the wear test extended rapidly due to higher contact stress. Then, the enlarging of the wear scar reduced gradually because the additive formed an effective tribofilm on the rubbing surfaces along with the contact stress reduced by the contact area extended. In addition, the results showed that PAG oil has good tribological performance in R134a refrigerant environment, and using the P-based EP additives in PAG oil could effectively improve the tribological performance of the PAG oil under extreme pressure condition.

INTRODUCTION

In air conditioner compressors, many components were often operated in an arduous lubricating condition and they were always operating in high contact pressure situation. However, these problems could be to result in reduced lifecycle of the components. Using a suitable additive could improve the extreme pressure (EP) performance of the lubricant and to reduce the wear behavior of the components, which operated under high contact stress condition. During lubrication operation, when the suitable oil and additive were used as the lubricant, an effectively protective tribofilm could be formed on the rubbing surfaces to avoid direct contact of the surface asperities on the surface and reduce the interference of them, decreasing the wear behavior. But in the more severe working environment, an oil film could not establish to effectively separate the rough rubbing surfaces. Especially in the case of high contact pressure, it was easy to make the lubricating regime into the boundary lubrication and prone to serious wear problems. In particular, line and point contact modes of the moving components, such as the gears and ball bearing elements always subjected to the extreme pressure problems at the contact region. Working at this condition, the extreme pressure performance of the lubricant is very important, and it must rely on the use of suitable additive to improve its EP performance. However, various additives have different functions, which were individually suitable working in the specific lubrication regimes. EP additives and anti-wear (AW) additives were separately used as the additives for the lubricant, which worked in the different conditions. The additives performance and protective mechanism in a tribosystem have been investigated with different experimental methods in many previous studies(Mistry, et al, 2013; Lin, et al, 2012; TADA, et al, 2016; Zulhanafi, et al, 2019; Piekoszewski, et al, 2001).

Molina. (1986) blending with the suitable additive to the lubricant could effectively improve the severe wear problem, which was always caused by boundary lubrication. Martin et al. (1986) and Johansson et al. (2014) research the EP additives typically have highly chemical reactivity with the rubbing surfaces. These constituent elements of the EP additive would decompose due to the high temperatures and pressure, which was caused by the

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rubbing process at high contact stress, and then formed a tribofilm on the contact surfaces to protect the rubbing surfaces. The tribofilm must possess sufficient shear strength to prevent the shear failure of the two contact surfaces to avoid more serious wear behavior. Fukui et al. (2000) and Tuomas et al. (2007) studied the four-ball tribometer to explore the performance of the additives in refrigerant environment, and the wear behavior of the specimens has been discussed at high contact pressure.

Nevertheless, the difference of EP and AW additives at extreme pressure conditions had not been explained detail, and the evolution of the wear scar was not fully discussed yet. According that, the object of this study is to clarify the difference of the tribological behaviors between AW and EP additives at extreme pressure condition in R134a environment.

EXPERIMENT

At extreme pressure condition, the tribological performance of the test oils, which contained different additives, was evaluated by four-ball sliding mode according to the dimension of the wear scar. Moreover, the evolution of the wear scar was monitored at the different sliding distance. The experimental conditions of the wear test were shown in Table 1. The temperature of the test oil was set at 62 ℃ in order to simulate the working condition of the scroll compressor. The specimen of four-ball test was made of AISI 52100 hardened steel with a diameter of 12.7 mm, and the surface roughness was R_a 0.01 μm. The PAG refrigeration oil was used as a base oil and its physical properties was shown in Table 2. Oleth-10 phosphorus (P)-based extreme pressure additive and Elco-102 zinc dialkyl dithiophosphates (ZDDP)-based anti-wear additive were used as the additives for the four-ball test. The test oils were constituted the PAG-based oil blended with 0.5% Oleth-10 and Elco-102 additives, respectively. The major physical properties of the additives are shown in Table 3.

Before wear test, the load cells were calibrated to ensure the data being reliable, and then set the load, speed and test duration required for the experiment. After the test balls and the jig set up, 15 ml test oil was poured into the oil cup and the R134a refrigerant was leaded into the oil cup with a flow rate of 80 ml/min. The schematic diagram of the four-ball test was shown in Fig. 1. The four-ball test conducted at different sliding distance in order to monitor the evolution of the wear scar in the different test oils. The oil temperature, load and friction force were recorded by a data acquisition system for the tribological performance analysis. The wear test of each condition was performed at least 3 times to confirm the repeatability of the experiment.

After wear test, the test ball was cleaned with ultrasonic cleaner in acetone for 40 minutes. Then, wear scar was observed and measured using an optical microscope (OM). The worn surface and the tribofilm were characterized by Field Emission-Electron Probe Micro-Analyser (FE-EPMA).

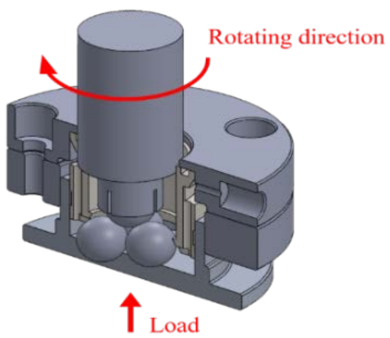


Fig.1. Schematic diagram of four-ball test.

Table 1. Wear test conditions

Parameter	Value
Load (N)	600
Oil Temperature (℃)	62
Rotational Speed (rpm)	1200
Sliding Speed (m/s)	0.4608
Refrigerant	R134a
Test duration (min)	3, 6, 10, 20, 30,40, 50, 60
Sliding Distance (m)	83, 166, 276, 553, 829, 1106, 1382, 1660

Table 2. Physical properties of PAG base oil

Parameter	Value
Viscosity @ 40℃ (cSt)	99
Viscosity @ 100℃ (cSt)	19.4
Viscosity Index	219
Pour Point (℃)	-42
Flash Point (℃)	226
Acid Number (mgKOH/g)	0.03

Table 3. Physical properties of the additive

RESULTS AND DISCUSSIONS

Apparent Contact Stress Evolution

Figs. 2 shows that the evolution of the apparent

Parameter	P-based	ZDDP
Type	EP	AW
Viscosity @ 40℃ (cSt)	1200	1000
Density @ 15℃ (g/cm)	1.06	1.2
Zinc (%)	x	10.6
Sulfur (%)	x	19.4
Phosphorus (%)	90	9.4
Test Concentration (wt%)	0.5	0.5

contact stress due to the enlarged of the wear scar at different sliding distances for the various test oils in the R134a environment at 600N and 62 °C. The apparent contact stress at each sliding distance was given by the applied load dividing by the area of the wear scar. The results indicated that the extreme pressure performance of P-based mixed oil exceed the other test oils. The P-based mixed oil can suffer the apparent contact stress approaching to 1628 MPa during a long period, the sliding distance from 1106 m to 1660 m, and the decrease trend of the apparent contact stress was slight when the sliding distance over 1106m. According that, the tribofilm formed by P-based additive could suffer higher contact stress than the others.

Nevertheless, the tribological performance of ZDDP mixed oil was less than the other test oils at the extreme pressure condition in the R134a refrigerant environment. Its tribological performance is even lower than that of the PAG-based oil. The apparent contact stress decreased rapidly before the sliding distance reached at 276 m. This phenomenon implied that the ZDDP mixed oil was unsuitable using at high contact stress condition in the R134a refrigerant environment. The result also implied that the compatibility of ZDDP additive and the PAG oil was not good in R134a refrigerant environment. The apparent contact stress of the ZDDP mixed oil at final state of 1660 sliding distance was approaching to 827 MPa.

For the PAG oil, the apparent contact stress was approaching to 1096 MPa at final state of 1660 sliding distance. Although the extreme pressure performance of the PAG oil was less than that of the P-based mixed oil, the tribological performance of the PAG oil was better than that of ZDDP mixed oil. This result indicated that the PAG oil was suitable for working in the R134a refrigerant environment.

During the wear test, the contact stress was very high at the initial stage of the four-ball wear test. Therefore, at this period the physisorption ability of the lubricant is very important. If the physisorption ability is insufficient, it will cause severe adhesive wear. When the wear scar was enlarged gradually, the real contact stress was reduced progressively. After that, local region could establish micro hydrodynamic pressure to support partial load. Farther, the temperature rise caused by rubbing effect, and then the additive decomposition to form chemisorption film that caused chemical reaction film formed on the rubbing surface to protect the surfaces from wear [7]. As mentioned above, the additive contributed to the tribological performance including physisorption film at low temperature and chemisorption film as well as chemical reaction film at high temperature. Because the physisorption film cannot suffer the high contact stress, the chemical reaction film formed by the additive was very important at extreme pressure condition.

Evolution of Wear Scar

During four-ball wear test, the evolution of the wear scar in the different test oils were displayed in Fig. 3, separately. The results show that PAG refrigerant oil has good compatibility with R134a that made it had good tribological performance in R134a refrigerant environment. Although the extension tendency of the wear scar in the PAG oil was obvious in the initial stage of wear test, it can be stabilized quickly and reduce the growth rate of wear scar. After the sliding distance over 553 meters, there was a significant growing trend of the wear scar again, in which the curve of the wear scar diameter evolution showed a step-like growth, but the range of variation is relatively small.

The growth rate of the wear scar diameter tested in the P-based mixed oil under the R134a refrigerant environment was slower than that of the other oils. The results showed that the tribological performance of the P-based mixed oil was excellent under extreme pressure condition in the R134a refrigerant environment than the others. The P-based mixed oil exerts its extreme pressure performance at the beginning of the four-ball test, which reduces the increase rate of the wear scar diameter. After the slip distance was over 1106 m, the wear scar diameter hardly extends because of the formation of the effective chemical reaction film. The removal of the tribofilm film could recover immediately, and then protected the rubbing surface to reduce the wear scar diameter effectively. That is the rate of the film formation has been balanced with the removal rate.

The evolution of the wear scar diameter of using the ZDDP mixed oil in the R134a refrigerant environment increased significantly at the initial stage even higher than that of the wear test in PAG oil. This result could implied that the chemical reaction film formation rate was slow, and the tribological performance of the PAG oil was faded when ZDDP additive was blended in the test oil. Another reason of this result may be caused by the strength of the chemical film of ZDDP being weak and accompanying with high chemical reaction rate to promote the corrosion wear. According that, ZDDP is not compatible with PAG oil in R134a refrigerant environment that made its extreme pressure performance be the worst among the test oils.

Figure 4 displays the wear scar evaluation, which tested in the different oils without R134a refrigerant. The results show that the wear scar at each sliding distance is the largest when the specimens tested in PAG base oil, comparing with the other oils. That implied that the extreme pressure performance of the PAG base oil the lowest among the test oils. The diameter of the scar extended quickly at the beginning of the wear test, and the wear scar diameter curve showed a step-like growth. It is because the worn surface at the beginning of the wear test is relatively rough causing by adhesive wear, and then the rough surface to result in the abrasive wear. Those effects of wear mechanism transfer got the high wear rate at wear test initial stage. After the initial stage, the contact area was enlarged to reduce the apparent contact stress reducing the wear rate. Moreover, ZDDP mixed oil can reduce the wear rate in the beginning of the wear test effectively, and reduce its growth of the wear scar diameter during the wear test. This result implied the tribofilm of the ZDDP can suppress the adhesive wear at the beginning of wear test. When the sliding distance over 1106 meters the growth of the wear scar was unobvious. The recovery rate of ZDDP tribofilm was quick enough to protect the wear surface effectively at this condition.

According to the above results, ZDDP is not compatible with R134a refrigerant that made extreme pressure performance of ZDDP mixed oil was the worst among the test oils in R134a environment.

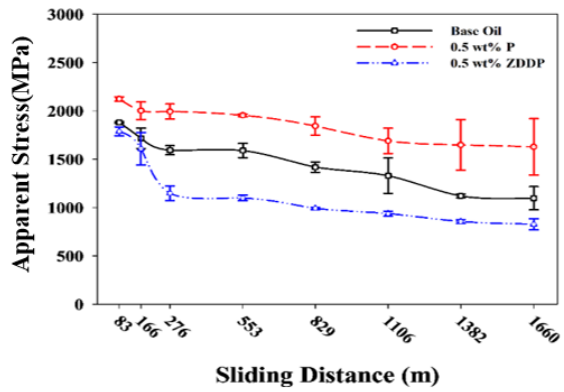


Fig. 2. Comparison of the evolution of apparent contact stress for the different test oils in R134a refrigerant environment at 600N and 62 °C.

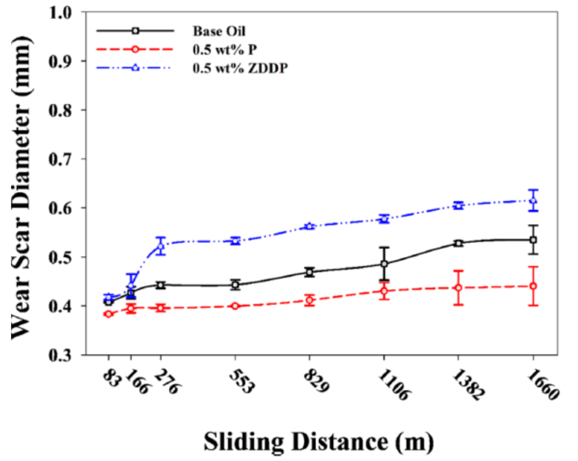


Fig. 3. Comparison of the evolution of wear scar diameter after the addition of different additives to PAG refrigeration oil in R134a refrigerant environment at 600N and 62 °C.

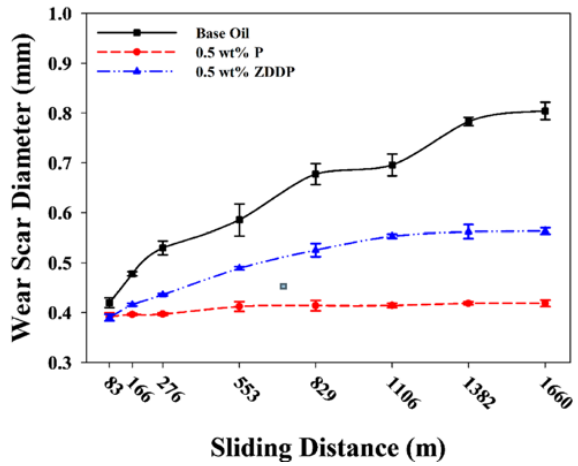


Fig. 4. The evolution of wear scar diameter tested in the different oils without R134a refrigerant at 600N and 62 °C.

Figure 5 shows that the evolution of the wear scar appearance at different sliding distances tested in the PAG base oil and the R134a environment. The wear scar enlarged significantly as the sliding distance increase, and it was observed that the wear scar extended outward from the center of the worn region.

Nevertheless, Fig. 6 shows that the evolution of the wear scar at different sliding distances tested in P-based mixed oil under the R134a refrigerant environment. The wear scar does not enlarge significantly at different sliding distances, which reduces effectively the tendency of the wear scar diameter to extend. It was due to the high temperature on the rubbing surface during the wear process such that the phosphorus-based additive reacted with the rubbing surface. Therefore, a phosphorus chemical reaction film can be formed on the rubbing surface to prevent the direct contact of the surfaces and improve the extreme pressure resistance effect.

Figure 7 shows the appearance of the wear scars, which tested in ZDDP mixed oil after sliding at different distances under the R134a refrigerant environment. The wear scar appearance has relatively rough and deep scratch. Additionally, when the sliding distance over 276m the wear scars of some specimens appear non-circle morphology, which was caused by the wear of the spinning ball.

Figure 8 shows that the evolution of the wear scar appearance at different sliding distances wear tested in the PAG base oil without R134a refrigerant. The results show that the formation of the wear scar during the wear test is rough, comparing with tested in the other oil, and the rough surface was formed by the relative sliding of the counter surface. The rough worn surface got severe abrasive wear and made the diameter of the wear scar extend rapidly.

Figure 9 shows that the evolution of the wear scar appearance at different sliding distances wear tested in the ZDDP mixed oil, it was also without R134a refrigerant. The figure showed that the diameter of the wear scar did not increase significantly when the sliding distance over 1106 meters, which indicates that the ZDDP tribofilm can recovery immediately and suffer the shear stress to protect the rubbing surface, so the wear scar did not grow up significantly. Additionally, some ZDDP chemical reaction films were detected at the outside of the rubbing zone. This phenomenon resulted from the accumulation of the scraped off chemical reaction film, and ZDDP tribofilm formed near the worn region due to the high temperature effect.

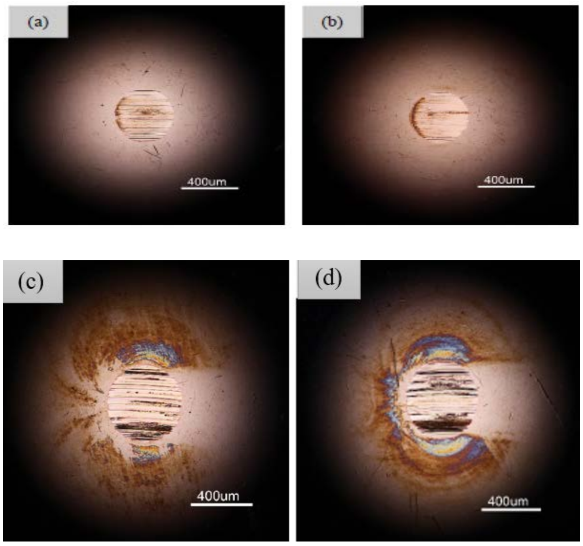


Fig. 5. evolution of wear scar in PAG oil under R134a refrigerant environment (a) 83 m (b) 166 m (c) 1106 m (d) 1382 m

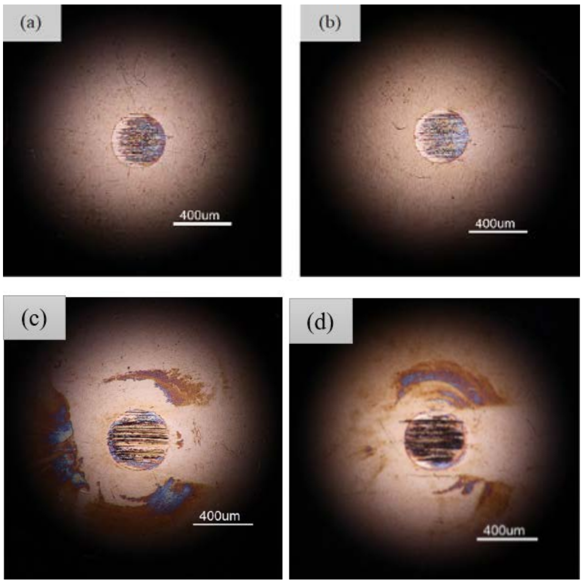


Fig. 6. Evolution of wear scar in P-based mixed oil under R134a refrigerant environment (a) 83 m (b) 166 m (c) 1106 m (d) 1382 m

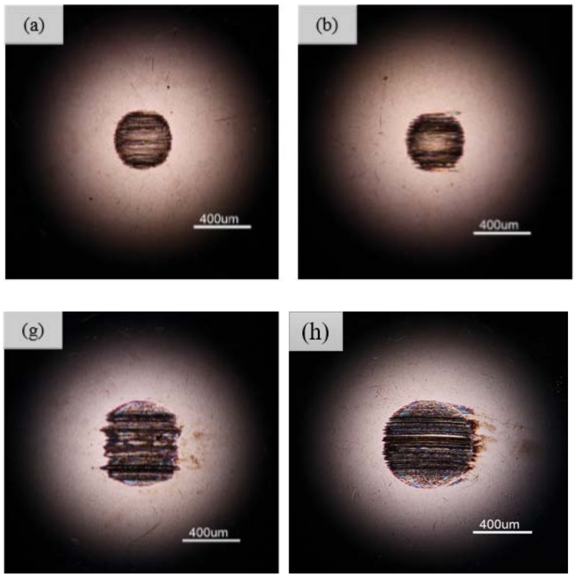


Fig. 7. Evolution of wear scar in ZDDP mixed oil under R134a refrigerant environment (a) 83 m (b) 166 m (c) 1106 m (d) 1382 m

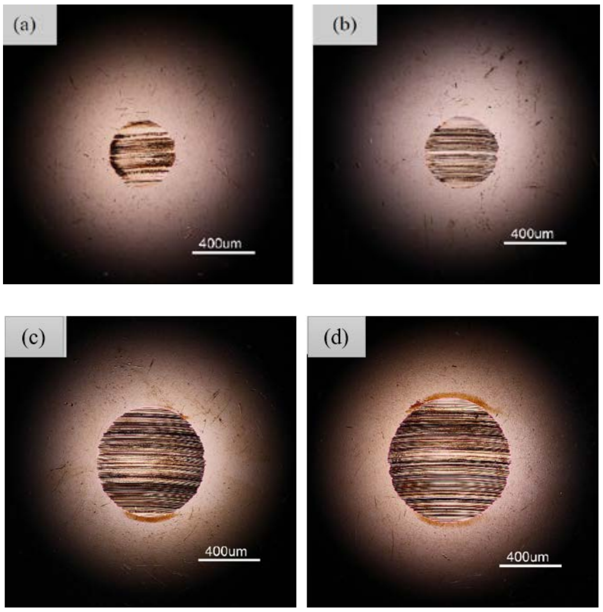


Fig. 8. Evolution of wear scar in PAG base oil without R134a refrigerant (a) 83 m (b) 166 m (c) 1106 m (d) 1382 m

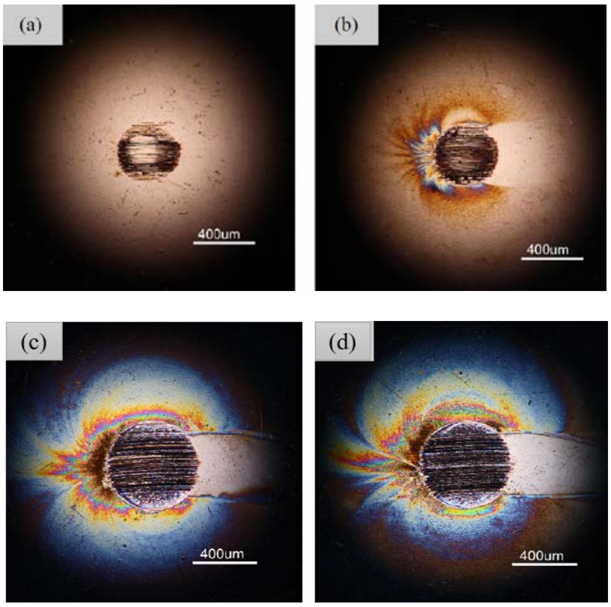


Fig. 9. Evolution of wear scar in ZDDP mixed oil without R134a refrigerant (a) 83 m (b) 166 m (c) 1106 m (d) 1382 m

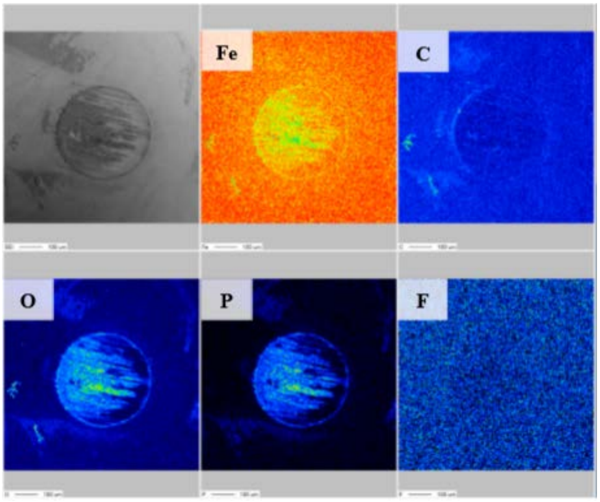
Electron Probe Micro Analysis of the Wear Scar

Figure 10 displays the results of EPMA characterizations of the worn surface after sliding at different sliding distances tested in P-based mixed oil under R134a refrigerant environment. The result shows that the tribofilm on the worn surface had a high intensity signal of phosphorus and oxygen elements at the beginning of the wear test. The contact temperature of the wear surface was increased rapidly due to the rubbing effect at high contact stress in the initial stage of the wear test. The temperature raising effect promoted the chemical reaction between the phosphorus-based additive and the substrate so that the phosphide film could form on the rubbing surface quickly to protect the sliding surface. At different sliding distances, the phosphorus film was always formed at the high contact stress region. The result also showed that the formation rate of the chemical film can compete with the removal rate of the material. That resulted in the phosphorus element can be detected by EPMA. When the formation rate of the chemical film could reach a balance with the removal rate of the material, and the strength of the chemical film is strong enough to withstand external contact stress. The additive can improve the extreme pressure performance effectively.

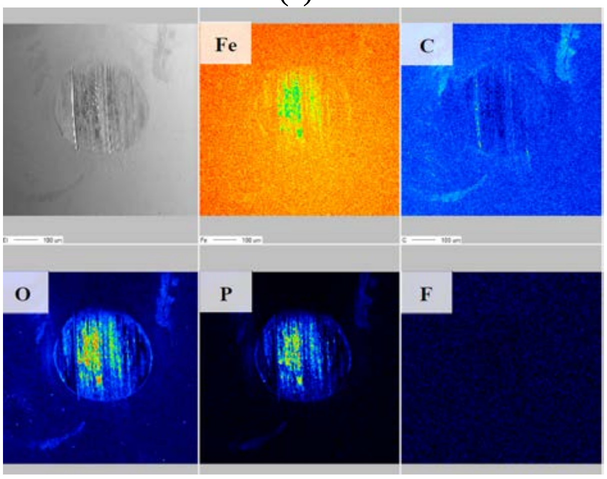
Figure 11 indicates the results of EPMA characterizations of the worn surface after sliding at different sliding distances tested in ZDDP mixed oil under R134a refrigerant environment. The results shows that S, P, Zn could be detected on the worn surface. Moreover, a little fluorine element was also detected on the worn surfaces, which sliding distances were 553 meters and 1660 meters.

Figure 12 shows the results of EPMA characterizations of the worn surface after sliding at different sliding distances tested in ZDDP mixed oil without R134a refrigerant. The results show that the zinc chemical reaction film can be easily removed due to its low shear strength. The chemical film contained with P or S element had high strength that can protect the sliding effectively and made P or S element can be detected in the worn surfaces.

In R134a refrigerant environment, the poor extreme pressure performance of ZDDP additive could be caused by two cases. One is the scrambling of the adsorption sits among ZDDP and the R134a refrigerant that impede the effective tribofilm formation on the rubbing surface. The other is that resulted from the R134a refrigerant to increase the chemical reaction rate of the ZDDP and form a tribofilm with weak strength that caused the partial corrosion wear and adhesion wear. It is an indirect evidence that the fluorine element of the R134a refrigerant could be detected on the worn surface.

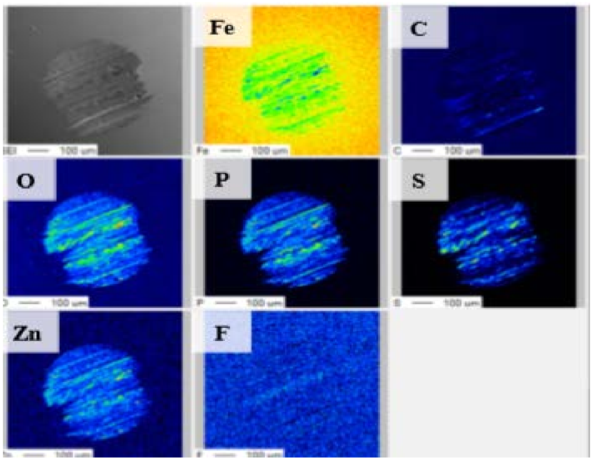


(a)

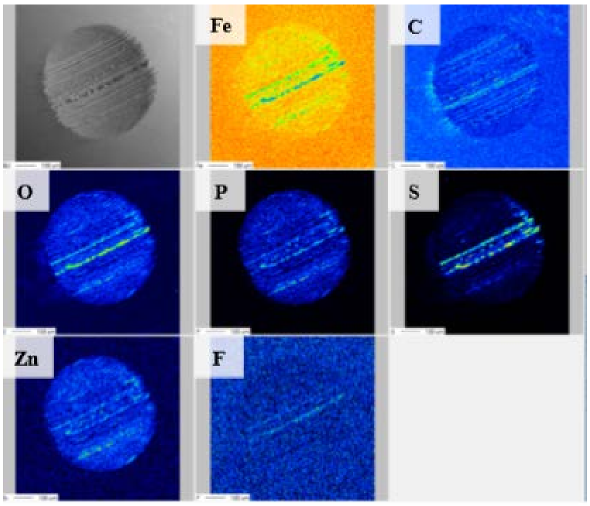


(b)

Fig. 10. EPMA surface analysis of wear scar evolution in P-based mixed oil under R134a refrigerant environment. (a) 553 m (c) 1382m

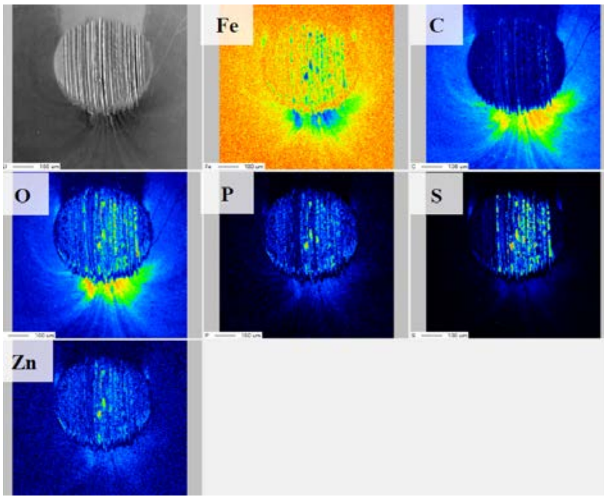


(a)

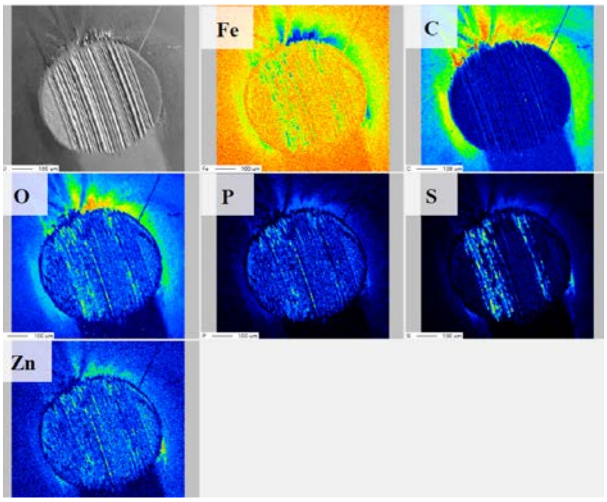


(b)

Fig. 11. EPMA surface analysis of wear scar evolution in ZDDP mixed oil additive under R134a refrigerant environment (a) 553 m (b) 1660m



(a)



(b)

Fig. 12. EPMA surface analysis of wear scar evolution in ZDDP mixed oil without R134a refrigerant (a) 553 m (b)1382m

CONCLUSIONS

The EP performance of refrigerant oil PAG and mixed oils, which contained with the different additives in PAG oil, were tested by the four-ball method in the R134a refrigerant environment. The wear scar evolution behavior and the tribofilm on the worn surface were discusses. Some important experimental results are as follows.

1. In R134a refrigerant environment or not, the phosphorus-based additive blending with refrigerant oil PAG can effectively improve the extreme pressure performance of the PAG oil, increased the sufferable ability of the apparent contact stress, and reduced the wear behaviour in the R134a refrigerant environment. When the tribofilm containing with phosphate formation on the rubbing surface, the rubbing surface can be protective effectively.
2. The ZDDP additive blending with refrigerant oil PAG can't improve the extreme pressure performance of the PAG oil in the R134a refrigerant environment effectively. This phenomenon may be caused by the scrambling among the adsorption sits among ZDDP and the R134a refrigerant that impede the effective tribofilm formation on the rubbing surface or the R134a refrigerant to increase the chemical reaction rate of the ZDDP and form a tribofilm with weak strength. However, the ZDDP additive can improve the extreme pressure performance of PAG oil effectively when the R134a refrigerant was absent.
3. The monitoring of wear scar evolution confirmed that the wear rate of four-ball test at the initial stage was very high, and then get it into a steady wear rate stage.
4. The monitoring of apparent contact stress evolution certified that various tribofilm had different EP performance. The high strength tribofilm can protect the rubbing surface at extreme pressure condition, had an excellent EP performance.

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不同添加劑加入PAG冷凍油進行磨耗試驗之磨疤演變

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摘 要

本文旨在探討不同添加劑的耐極壓性能，並觀察在PAG潤滑油中加入不同類型添加劑之四球磨耗的磨疤直徑演變。使用硬化鋼球和R134a 製冷劑進行了四球滑動磨損測試，以模擬空調壓縮機的內部環境。實驗結果表明，由於較高的接觸壓力，磨損試驗初期的磨損痕跡迅速擴展。然而，在潤滑劑和添加劑在摩擦表面上形成化合膜後，磨疤直徑的增大逐漸減小。此外，結果表明，PAG 油在 R134a 製冷劑環境中具有良好的摩擦學性能，並且在 PAG 油中使用磷系添加劑可以有效改善潤滑油在極端壓力條件下的性能.