Asian Journal of Chemistry; *Vol. 24, No. 10 (2012), 4507-4510*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Tribological Study of a Non-N, P-Containing Acetic Ester Derivative as Additive in Hydrogenated Oil

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(*Received*: 5 August 2011; *Accepted*: 7 May 2012) AJC-11423

A novel ester derivative, octyl xanthate acetic octcyl xanthate ester (XE) was synthesized and it's tribological behaviours as additive in hydrogenated oil, were evaluated using a four-ball tester. Results show that the compound possesses good antiwear performance, extreme pressure capacity and good friction-reducing property. The action mechanism was estimated through analysis of the worn surface with X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). The results of XPS and SEM analyses illustrate that the prepared compound as an additive in hydrogenated oil forms a protective film containing ferric sulfide and ferric sulfate compounds on the rubbed surface.

Key Words: Acetic ester derivative, Additive, Hydrogenated oil, Tribological mechanism.

INTRODUCTION

It is well-known that additive[1] is a essential component for lubricant and it play an improtant role for ensuring lubricant capability and satisfing specific requirement.

Sulfuration alkene is a very important extrement pressure additive and it can offer effective protect for qear and axle, in order to avoid tiredness, sinter and worn of machine, it had been used in gear oil. When sulfuration alkene was mixed with P-containing additive (such as dibuthylphosphate), it will easy produce mercaptan smell[2] and the mercaptan is damage for human and environment, so that confined it's business application in some degree.

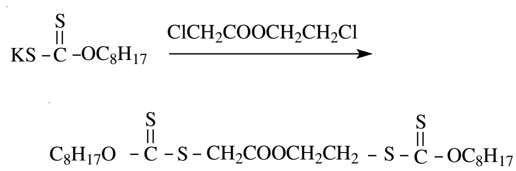
Xanthate group contains sulphur element. Many results showed that sulphur[3] can improve lubricating oil extreme pressure capability. The C-S bind energy of xanthate is more than that of sulfuration alkene[1] and that made it has higher temperature stability and lower corrosivity. Even it possesses friction-reducing and antioxidation multifunction capability and substituting sulfuration alkene aim will be realize by using S-containing compound. It will increase the extreme pressure and antiwear property by introducing the xanthate group into ester compound. The anioxidation of base oil is decreased after hydrogrnated, the xanthate can improve base oil antioxidation capability.

In the paper, a kind of xanthate as raw material, to synthesize a kind of xanthate-containing ester derivative, which accord with biodegradable request of lubricating oil additive. The tribological behaviours of synthetic ester derivative as additive in hydrogenated oil were evaluated with a four-ball machine. The tribological mechanism was discussed by analysis of solid film structure of rubbed surface using XPS and SEM.

EXPERIMENTAL

Lubricating oil and additives: A commercial hydrogenated oil product 5 Cst, which $\nu_{100\,°C}$ is 5.539 mm^2 s^{-1}, flash point is 238 ºC, viscosity coefficient is 110, made by Daqing Refinery Factory of China, was used as the lubricating oil without any further treatment.

The aimed compound (xanthate ester) was synthesized according to the pathway outlined in **Scheme-I**.



Scheme-I: Reaction pathway of novel compounds

The product were characterized by IR and elemental analysis. The elemental analysis results were that C was 53.79 (53.23), H was 8.19 (8.06), S was 24.99 (25.81), values in parentheses were calculated and that are in good agreement with the required values within the limits and experimental error of lubricating oil additives.

Specimens and testing apparatus: The wear properties of the ester derivative in hydrogenated oil were evaluated with a four-ball machine at a rotating speed 1450 rpm, test duration of 0.5 h and room temperature. The balls used in the tests were made of GCr15 bearing steel (AISI52100) with an HRC of 59-61. The load-carrying capacity of the additive was obtained according to GB3142-82, similar to ASTM D-2783. An optical microscope was used to determine the wear scar diameters of the three lower balls with an accurate reading to 0.01 mm. Then, the average of the three wear scar diameters was calculated and cited as the wear scar diameter reported in this paper. The friction coefficients were recorded automatically with a self-recording apparatus with the four-ball tester. Before each test, the specimens were cleaned in petroleum ether, then dried.

Worn surface analysis: X-Ray photoelectron spectroscopy (XPS) was conducted with a PHI-5702 X-ray photoelectron spectrometer. The upper ball used for XPS analysis was washed ultrasonically with petroleum ether and dried after testing at additive concentration of 2.0 wt. % under load of 392 N for test duration of 0.5 h. The MgK_α radiation was used as the excitation source at pass energy of 29.35 eV and the binding energy of C1s (284.6 eV) was used as the reference. The wear scar morphology was visualized with JEM-1200EX scanning electron microscopy at voltage 20 kV, to study the rubbed surface morphology.

RESULTS AND DISCUSSION

Maximum non-seizure load (PB value): The maximum non-seizure load (PB value) of base oil (5Cst) and different concentration additives in 5Cst were shown on Table-1.

TABLE-1
MAXIMUM NON-SEIZURE LOAD (P_B VALUE) OF DIFFERENT CONCENTRATION ADDITIVE

Additive	5Cst	1.0 %	2.0 %	3.0 %
P_B value (N)	392.3	588.4	646.8	706.1

The results show that the PB values of the compound in different concentrations are much higher than that of base oil and the PB value increases with the additive concentration increasing. This indicated that the synthesized compound has excellent load-carrying capacity.

Friction-reducing performance: The friction coefficient of synthesized compound in seven different concentrations under 392 N and different applied loads at the additives concentrations 2 wt % are shown in Fig. 1.

The friction coefficient decreased with the applied load increasing. It means that the xanthate-containing ester additives possess friction-reducing behaviour at long range applied load.

The friction coefficient of the 5Cst was 0.113 under the applied load 392 N, but it was reduced 13.3 % to 0.107 by the addition of 2.0 wt % additive. With the higher of additive concentration, the friction coefficient increased. The decreasing of friction coefficient can be attributed to the formation of

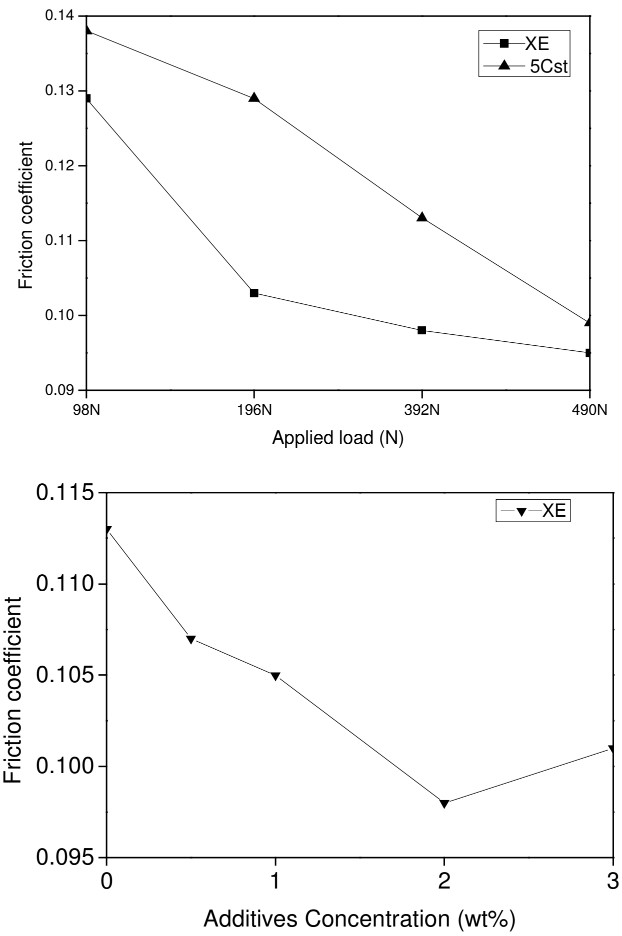
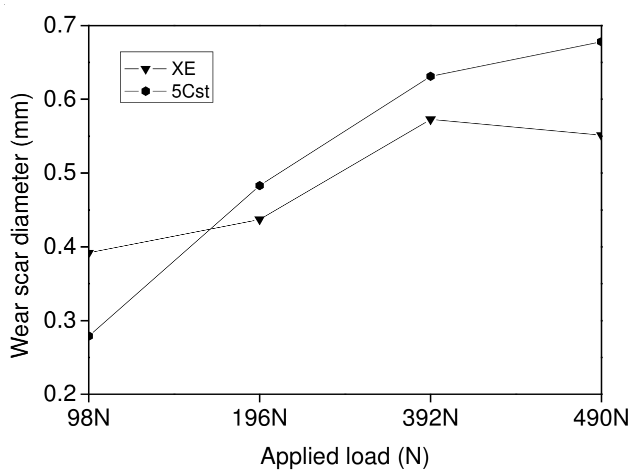


Fig. 1. Friction coefficient of various applied load and additive concentration

adsorption film and/or reaction film by the additive on the rubbing surface[4]. The more novel additive is added, the more molecular layers within the adsorption film and more reaction products are generated to prevent the asperities on the rubbing surfaces from direct contact and the lower the friction coefficients become. When the concentration arrives at some degree, the adsorption process tends to be saturated, it will not add the adsorption of additive.

Antiwear performance: Fig. 2 gives the wear scar diameter (WSD) as the function of the additive concentration at the applied load at 392 N and applied load at the additives concentration 2 % in base oil.



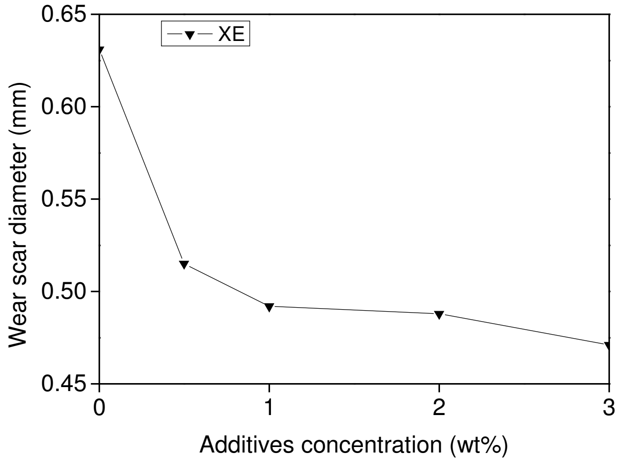


Fig. 2. Variations in the wear scar diameter with concentration and applied load (N)

The results indicate that the additive exhibit good antiwear properties in a wide range of applied load. The wear scar diameter increases with the applied load from 98 N to 490 N.

It can be seen that the addition additive in base stock significantly reduce the wear scar diameter, this results indicate that the novel xanthate-containing ester additive has excellent antiwear property. The lower WSD is obtained along with additive concentration increasing. With the increasing of additive concentration, the S content is increased, the antiwear capability is increased. It is due to the protective film formed by the additives and its decomposers on the sliding surface under the boundary tribological conditions.

Discussion of tribology mechanism of novel additive: The enlarged SEM photographs is shown in Fig. 3.

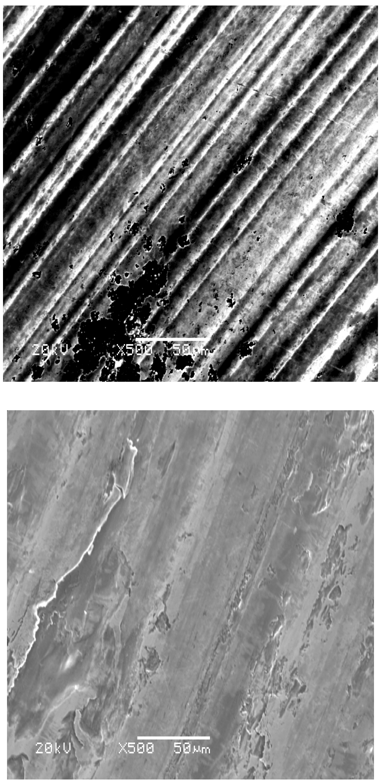
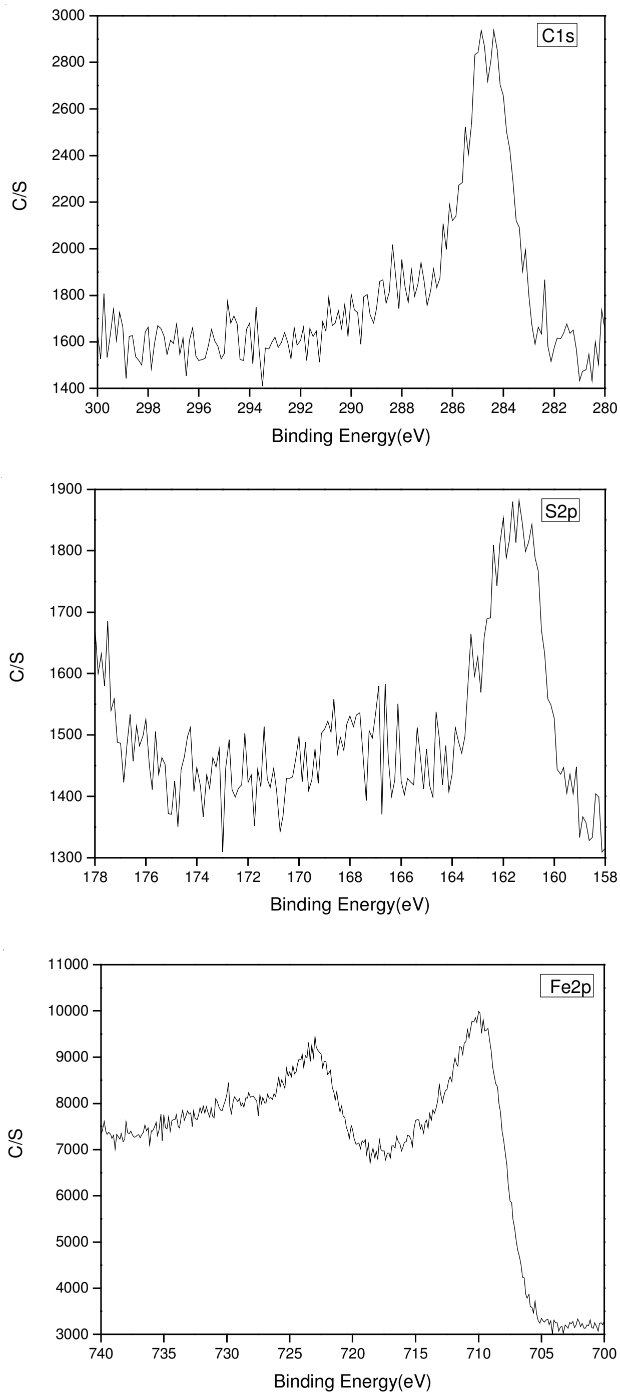


Fig. 3. SEM morphologies of worn surface lubricated with 5Cst (left) and 2.0 wt % XE (right) under 392 N

It indicate that severe scuffing occurs with lubrication of 5Cst alone, taking on grain abrasion characteristic, while only slight frictional tracks appear with lubrication of xanthate ester and there has appeared some layer structure matter, which assuming the characteristics of corrosive worn. It may be the novel S element had reacted with the metal surface during the friction process, generating chemisorption. And it is generally accepted that the tribological behaviours of additive are closely related to the performance of the protective film formed by physisorption, chemisorption and tribochemical reaction during the process.

In order to explore the lubricating mechanism of the additive in hydrogenated oil, XPS analysis of the worn surface was carried out and the analysis results are shown in Fig. 4.



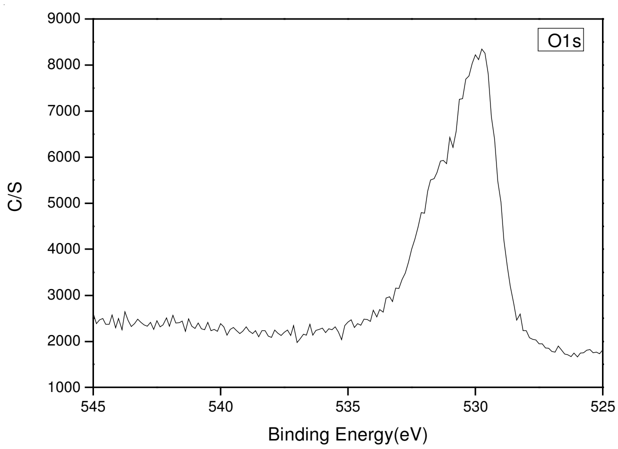


Fig. 4. XPS spectra of C_{1s}, S_{2p}, Fe_{2p}, O_{1s} (2.0 wt % XE/5Cst)

The spectrum of S_{2p} of HXAE illustrates[5] the existence of peak at 168.8, 170.0 and 171.2 eV which corresponds to ferric sulfide, ferric sulfate and organicsulfur compound on the worn scar, showing the tribochemical reaction that occurred between the additive with the metal surface during the sliding processes. The Fe_{2p} peak appearing at binding energy 711.2 and 724.7 eV, corresponds to iron oxide and/or sulfide, indicating that the lubricated steel surface is liable to oxidize or sulfurize in the friction process. The O_{1s} peak corresponding to iron oxide appears at 533.4 eV and means that it had occurred tribochemical reaction between the additive and steel ball surface during the lubricating process.

Surface analysis results demonstrate that the synthesized additive molecules maybe decomposed[6] to produce $(RO)_2CS(S)H$ (or other SH compound), so a stable lubricating film can be formed on the rubbed surface. This lubricating film is complex and consists of reaction layer and adsorption layer. The reaction layer originates from the tribochemical reaction of S element contained in the xanthate group, which can easily interact with the freshly metal surface to form extreme pressure and antiwear surface film[7] which containing $FeSO_4$ and/or FeS. Products of tribochemical reactions between additives and metal surface can be transformed to an adherent antiwear surface film, which can prevent the direct contact of metal and metal, to reduce the metal stock abrasion. With such stable reaction and adsorption layers, the novel additive can effectively decrease the friction and wear and possesses excellent tribological performances.

Conclusion

From the above results, the following conclusions can be drawn: The synthesized ester derivative as additives in 5cst base oil show excellent load-carrying capacity and improve the antiwear and friction-reducing behaviour at appropriate concentrations. The friction-reducing and antiwear behaviour of the additive are sensitive to weight concentration and applied load. Through the SEM and XPS analysis results, the synthetic additive function to reduce friction and wear of steel-steel sliding system by chemical adsorption on and tribochemical reaction with the steel surface. The protective film formed during sliding processes contributed to the increase in the wear resistance and friction reduction.

ACKNOWLEDGEMENTS

This work is supported financially by the Chinese Natural Science Foundation (No. 21063007); Jiangxi Provincial Natural Science Foundation (No. 2010GZH0030); Jiangxi Provincial Science and Technology Department Projects of China (No. 2010BGB00602) and Jiangxi Education Department Foundation of China (Grant No. GJJ10442).

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