

XANES Study of Tribofilms

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Introduction

Zinc dialkyl dithiophosphate (ZDDP) is an excellent anti-wear additive and helps extend the life of engines. ZDDP works by breaking down and forming metallic glass films composed of P, S, O, Zn and Fe on the tribosurfaces, in addition to forming protective organic polyphosphate films on the surface. Unfortunately, over time these films also decompose and result in the formation of free P and S that move downstream in the engine and deposit on the surface

of catalytic converters. Heavy metal deposits such as Zn also reduce the efficiency of catalytic converters resulting in increased harmful emissions. In this study two approaches have been used to enhance the quality of tribofilms using ashless (without Zn) antiwear agents as well as ZDDP coupled with fluorinated hydrocarbons.

Science

Antiwear agents used in this study, including short chain and long chain ashless dialkyl dithiophosphates and a mixture of amine phosphates that do not contain any Zn, have the potential to reduce the extent of heavy metal deposits on a catalytic converter. In this study two approaches have been explored: (1) the use of ashless antiwear agents to eliminate the use of Zn; and (2) the use of polytetrafluoroethylene as an additive to enhance the wear performance so that smaller amounts of ZDDP may be used.

A significant portion of wear in an engine occurs during start up when all the oil is located in the pan and during periods of rapid acceleration. At these times the point of contact is starved for lubricant and lubrication falls in the boundary regime when the potential for metal on metal contact exists. At this point of time the only protection from catastrophic wear is the presence of a very wear resistant amorphous tribofilm on the surface that is approximately 100-200 nm thick. In the current experiments, boundary lubrication tests were conducted in the presence of limited amounts of oil to develop a stable tribofilm on the surface. All of the wear tests were conducted at a load of 24 kg (12.5 mm WC ball in contact with a 50 mm diameter ring made up of 4140 steel rotating at 700 rpm). The wear tests were conducted for a duration of 15,000 cycles. Once the wear tests were complete the rings were cut using a low speed diamond saw using a pure mineral oil lubricant to prevent thermal damage and contaminants from getting on the wear surface. The cut rings were stored in desiccators until they were ready for observation. Prior to observation the wear track was cleaned

with acetone to remove any residual mineral oil deposits and mounted in the PGM beamline 11ID-2. The P and S *L*-edge spectra were recorded, however for the sake of brevity this report primarily reports the characteristics of the phosphorous compounds formed in the tribofilms.

Discussion

In order to characterize tribofilms that form on the surface model compounds have to be examined. In particular earlier studies by Kasrai and co-workers using ZDDP have established the presence of phosphates of Zn and Fe in the tribofilms. In addition, it has been shown by them that several short and long chain polyphosphate compounds are possible in the tribofilms. Figure 1 shows P *L*-edge for several different phosphates of Zn.

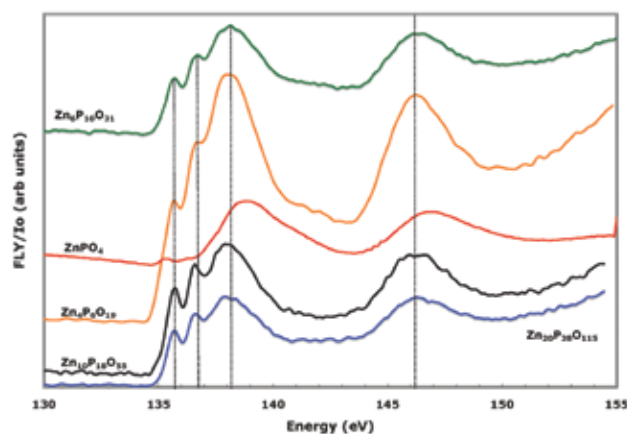


Figure 1: Phosphorous *L*-edge normalized fluorescence yield spectra of various short chain and long chain polyphosphates of Zn. Zn polyphosphate data courtesy of Dr. Masoud Kasrai [1].

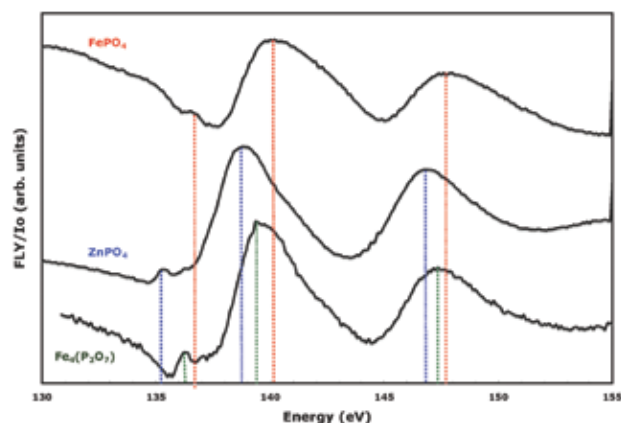


Figure 2: Phosphorous *L*-edge normalized fluorescence yield spectra of FePO_4 , $\text{Zn}_3(\text{PO}_4)_2$ and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ standards.

Comparison of Figures 1 and 2 indicates that the P *L*-edge is shifted to higher energy in FePO₄ compared to Zn₃(PO₄)₂. The P *L*-edge of Fe₄(P₂O₇)₃ is shifted to lower energy compared to FePO₄ but is still higher than Zn₃(PO₄)₂. On the other hand, longer chain Zn-phosphates have their P *L*-edge peaks shifted to lower energies compared to Zn₃(PO₄)₂ and in addition have some distinctive fine structure near the edge.

Three different organophosphate compounds were examined. Two were ashless organo thiophosphate compounds, one made with short chain alcohol (resulting in higher volatility) and the other with long chain alcohol (with higher stability), the last antiwear compound was a mixture of amine phosphate.

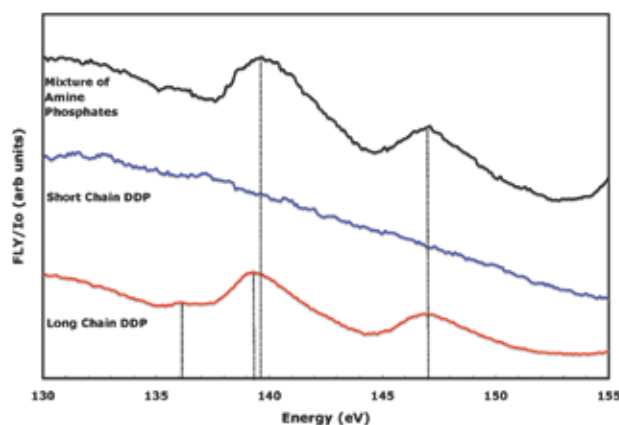


Figure 3: Phosphorous *L*-edge spectra from tribofilms from three ashless antiwear chemistries.

Comparison of Figures 2 and 3 indicate that the phosphorous is present in the form of iron phosphates when long chain DDP is used as an antiwear agent. Closer examination of the spectra indicates that the phosphates are present as short chain polyphosphates of Fe of the form Fe₄(P₂O₇)₃ rather than FePO₄. Comparison of the spectra formed with short chain DDP with the spectra from long chain DDP under boundary lubrication indicates that the more stable long chain ashless DDP forms a stable tribofilm while the short chain DDP being more volatile does not form a stable tribofilm on the surface. Tribofilms formed by using a mixture of amine phosphates indicate that the tribofilm is constituted of FePO₄ compared to Fe₄(P₂O₇)₃ in the case of long chain DDP. The Fe₄(P₂O₇)₃ is more stable and affords better wear protection in comparison to tribofilms with FePO₄. This is reflected by the better wear protection under tribological conditions with long chain DDP in comparison to a mixture of amine phosphates.

PTFE is a super hydrophobic polymer that has the potential to reduce friction and improve wear performance. However, little is known as to the exact mechanism by which tribofilms formed with PTFE and ZDDP differ from films formed with ZDDP alone. In this study tribofilms were formed under boundary conditions for the two chemistries and examined using XANES. Examining the spectra in Figure 4, it is evident that there are no major differences in the nature of the phosphates formed when PTFE is added to ZDDP with the exception that some

additional fine structure is present near the edge in the presence of PTFE. Examining the position of the primary P *L*-edge peak it is also evident that in both cases phosphates that are present are Fe₄(P₂O₇)₃ and not Zn-polyphosphates. This indicates that under extreme pressure and boundary lubrication conditions, Zn-polyphosphates do not form in the tribofilms. In addition in the presence of PTFE it is evident that the fine structure characteristic of Fe₄(P₂O₇)₃ is more prevalent compared to ZDDP.

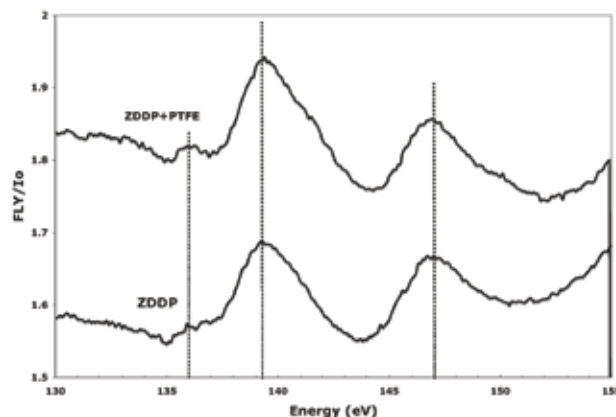


Figure 4: Phosphorous *L*-edge spectra from tribofilms from ZDDP and ZDDP with PTFE.

Conclusion

When ashless antiwear agents are used under tribological conditions, the use of longer chain DDP results in better wear performance by the formation of Fe₄(P₂O₇)₃ in the film in comparison to a mixture of amine phosphates when the primary phosphate is FePO₄. Shorter chain DDP antiwear agents do not perform well under boundary lubrication under extreme pressure. When PTFE is used along with ZDDP under tribological conditions, the tribofilms chemistry in both cases is largely Fe₄(P₂O₇)₃ with more evidence of short chain iron phosphates in the presence of PTFE. Future work includes examining additional ashless thiophosphate compounds under boundary conditions and the role played by antioxidants on the formation and chemistry of tribofilms. In addition, we plan to examine films formed under thermal and thermo-oxidative conditions to distinguish them from tribofilms and gain a better understanding of the mechanism of formation of these films and their properties.

References

1. Kasrai, M. 2007, Personal Communication
2. Nichols, M.A., Do, Than, Norton, P.R., Kasrai, M, Bancroft, M.G. 2005, "Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates" *Tribology International*, 38, 15-39.

Acknowledgements

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