ZDDP DEGRADATION AND TRIBOCHEMISTRY REVEALED BY MASS SPECTROMETRY

C. Gabler^a, J. Brenner^a, M. Frauscher^{a,b}, A. Grafl^a, N. Dörr^{a*}

*nicole.doerr@ac2t.at ^aAC2T research GmbH, Viktor-Kaplan-Str. 2C, 2700 Wiener Neustadt, Austria ^bVienna University of Technology, Institute of Chemical Technologies and Analytics Getreidemarkt 9/164 1060 Wien, Austria

KEYWORDS

Boundary lubrication;zinc dialkyldithiophosphate (ZDDP);oxidation;mass spectrometry (MS);X-ray photoelectron spectroscopy (XPS)

ABSTRACT

Tribochemistry of ZDDP antiwear additives is reported by numerous publications, e.g., comprehensively summarised in a review by Spikes [1]. For tribofilmcharacterisation, secondary ion mass spectrometry (SIMS) is known forharsh ionization, hence connected with significant loss of molecular info. For the identification of ZDDP degradation products in lubricants, chromatography and nuclear magnetic resonance (NMR) spectroscopy, particularly ¹P-NMR, are known [2].

To overcome the limitations to satisfactorily describemechanisms of ZDDP degradation and tribochemistry on the molecular level, an analytical approach based on MS is proposedjoining findings from oil degradation and ZDDP tribochemistry [3-4].

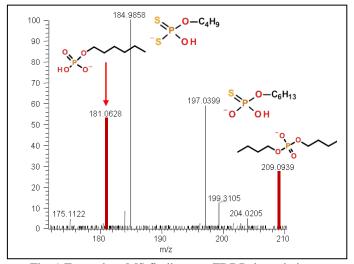


Fig. 1 Exemplary MS findings on ZDDP degradation – comparison of fresh and used oil – red bars indicate ZDDP degradation products only found in the used oil [5]

Used oils generated by oxidative and/or tribologicalstress were characterised fordegradation products using highly accurate MS and compared with fresh oil for a proper description of the used oil condition. Mass spectra disclosed the formation of alkyl phosphates in used oils originating from ZDDP (Fig. 1). It could be also shown that the fresh oil can contain ZDDP derivatives, being either by-products or oxidation products.

The findings from oil chemistry were connected with tribological performance assessed in an oscillating steel-steel contact. Mapping of the wear scars with MS and XPS revealedspecific distribution patterns of organic and inorganic moieties on the surface that account for the local tribological conditions along the disc wear scar.

ACKNOWLEDGMENTS

This work was funded by the Austrian COMET-Program (Project XTribology, no. 849109) and the work was carried out at the "Excellence Centre of Tribology" (AC2T research GmbH).

REFERENCES

- [1] Spikes, H., "The history and mechanisms of ZDDP,"Tribol Lett, 17, 3, 2004, 469-489.
- [2] Barnes, A.M., Bartle, K.D. and Thibon, V.R.A., "A review of zinc dialkyldithiophosphates (ZDDPS): characterisation and role in the lubricating oil,"Tribol. Int., 34, 6, 2001, 389-395.
- [3] Gabler, C., Pittenauer, E., Dörr, N. and Allmaier, G., "Imaging of a Tribolayer Formed from Ionic Liquids by Laser Desorption/Ionization-Reflectron Time-of-Flight Mass Spectrometry,"Anal. Chem., 84, 24, 2012, 10708-10714.
- [4] Pisarova, L., Totolin, V., Gabler, C., Dörr, N., Pittenauer, E., Allmaier, G. and Minami, I., "Insight into degradation of ammonium-based ionic liquids and comparison of tribological performance between selected intact and altered ionic liquid," Tribol. Int., 65, 2013, 13-27.
- [5] Repka, M., Dörr, N., Brenner, J., Gabler, C., McAleese, C., Ishigo O. and Koshima M., "Lubricant-surface interactions of polymer-coatedengine journal bearings,"Tribol. Int., 109, 2017, 519-528.