

# Chemical State and Structural Evolution of Metal-Containing Additives in Engine Oil under Different Operating Conditions

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Metal-containing additives are indispensable components of modern engine oils, providing antiwear, friction-modifying, detergent and antioxidant functions. Among them, zinc dialkyldithiophosphate (ZnDTP) is one of the most widely used antiwear additives. During engine operation, however, additive-derived species are expected to undergo chemical transformations, which can influence lubricant performance and durability. Although the degradation behavior of lubricant additives has been widely studied, the evolution of ZnDTP-derived species in actual engine oils has not been fully understood.

In this study, ZnDTP-derived species in engine oils were investigated using Zn K-edge X-ray absorption fine structure (XAFS) spectroscopy and <sup>31</sup>P nuclear magnetic resonance (<sup>31</sup>P-NMR) spectroscopy. Three oils were analyzed: fresh oil (FO), used oil collected after engine operation (UO), and water-added oil (WAO) prepared by adding a prescribed amount of water to UO. Water contamination is recognized as a potential issue in modern engine lubrication systems because operating conditions that suppress oil temperature rise can promote water accumulation in engine oils. Therefore, WAO was prepared to evaluate the influence of water contamination on the chemical evolution of ZnDTP-derived species.

Zn K-edge XAFS measurements were performed to investigate chemical states and local structures of ZnDTP-derived species directly in engine oils without pretreatment. In particular, the X-ray absorption near-edge structure (XANES) region, which is sensitive to oxidation state and local coordination environment, was analyzed. Figure 1 shows Zn K-edge XANES spectra of FO, UO and WAO. Compared with FO, both UO and WAO exhibited shifts of the absorption edge toward higher energies, indicating significant changes in Zn coordination environments. Furthermore, differences in white-line intensity and peak position suggest distinct Zn species among the three oils. The results of linear combination fitting (LCF) are summarized in Figure 2. FO was dominated by the FO component, whereas phosphate-related Zn species became dominant in UO. In contrast, WAO showed a significant increase in Zn<sup>2+</sup>-like species. These results suggest that ZnDTP-derived species are transformed into Zn-O-P-containing phosphate structures during engine operation and subsequently undergo additional chemical changes in the presence of water.

Although XAFS is a powerful technique for investigating chemical states and local structures of metal species, its application to formulated lubricants has been limited because of the complexity of oil compositions and the relatively low concentrations of additive-derived elements. In the present study, Zn K-edge XAFS successfully captured condition-dependent changes in ZnDTP-derived species and provided direct information on the transformation of Zn coordination environments during service and water exposure.

Complementary <sup>31</sup>P-NMR analysis revealed the formation of polyphosphate-like species in UO and an increase in orthophosphate species in WAO. The XAFS results demonstrated changes in Zn coordination environments, whereas <sup>31</sup>P-NMR provided information on phosphate speciation and polymerization states. Combining the two techniques suggests that Zn-containing polyphosphate-related structures formed during engine operation are partially hydrolyzed in the presence of water, accompanied by an increase in ionic Zn species.

The present results indicate that ZnDTP-derived species initially containing Zn–S coordination are transformed into Zn–O–P-containing phosphate structures during engine operation. Furthermore, water contamination promotes hydrolysis of these phosphate-related structures, resulting in the formation of lower-polymerized phosphate species and an increase in Zn<sup>2+</sup>-like species. The combination of Zn K-edge XAFS and <sup>31</sup>P-NMR provides complementary information on Zn coordination environments and phosphate speciation, demonstrating an effective approach for investigating degradation processes of ZnDTP-derived species in operating engine oils.

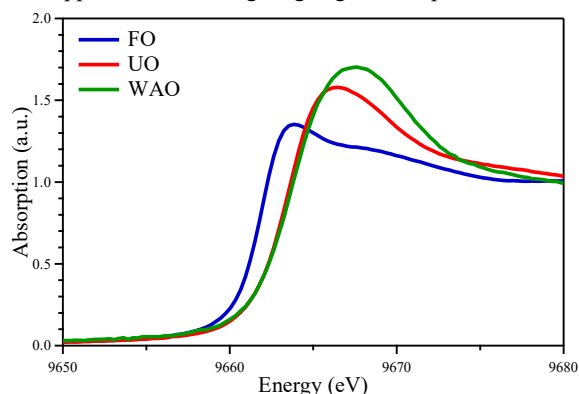


Fig. 1 Zn K-edge XANES spectra of FO, UO, and WAO.

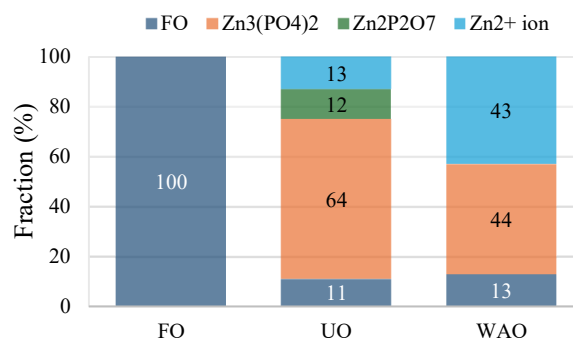


Fig. 2 Relative fractions of Zn species estimated by linear combination fitting (LCF) of Zn K-edge XANES spectra.