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## Effective Medium Approximations for Modeling Ellipsometric Responses from Zinc Dialkyldithiophosphates (ZDDP) Tribofilms Formed on Sliding Surfaces

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Abstract: Sliding lubricated surfaces induce the formation of tribofilms that reduce friction, wear and prevent large-scale damage of contact parts. Engine oils and lubricants use antiwear and antioxidant additives such as zinc dialkyldithiophosphate (ZDDP) from where protective tribofilms are formed by degradation. The ZDDP tribofilms are described as a two-layer structure composed of inorganic polymer material. On the top surface, the long chain polyphosphate is a zinc phosphate and in the bulk, the short chain polyphosphate is a mixed Fe/Zn phosphate with a gradient concentration. The polyphosphate chains are partially adherent to steel surface through a sulfide and work as anti-wear pads. In this contribution, ZDDP tribofilms formed on gray cast iron surfaces are studied. The tribofilms were generated in a reciprocating sliding tribometer with a piston ring-cylinder liner configuration. Fully formulated oil of SAE grade 5W-30 was used as lubricant during two tests at 40Hz and 50Hz. For the estimation of the tribofilm thicknesses, spectroscopic ellipsometry was used due to its high accuracy and nondestructive nature. Ellipsometry works under an optical principle where the change in polarisation of light reflected by the surface, is associated with the refractive index of the surface material or to the thickness of the layer deposited on top. Ellipsometrical responses derived from tribofilms are modelled by effective medium approximation (EMA), which includes the refractive index of involved materials, homogeneity of the film and thickness. The materials composition was obtained from xray photoelectron spectroscopic studies, where the presence of ZDDP, O and C was confirmed. From EMA models it was concluded that tribofilms formed at 40 Hz are thicker and more homogeneous than the ones formed at 50 Hz. In addition, the refractive index of each material is mixed to derive an effective refractive index that describes the optical composition of the tribofilm and exhibits a maximum response in the UV range, being a characteristic of glassy semitransparent films.

**Keywords:** effective medium approximation, reciprocating sliding tribometer, spectroscopic ellipsometry, zinc dialkyldithiophosphate

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