Binary additive mixtures of phosphonium ionic liquid (IL-P) with soluble boron (SB) additives as high performance antiwear additives

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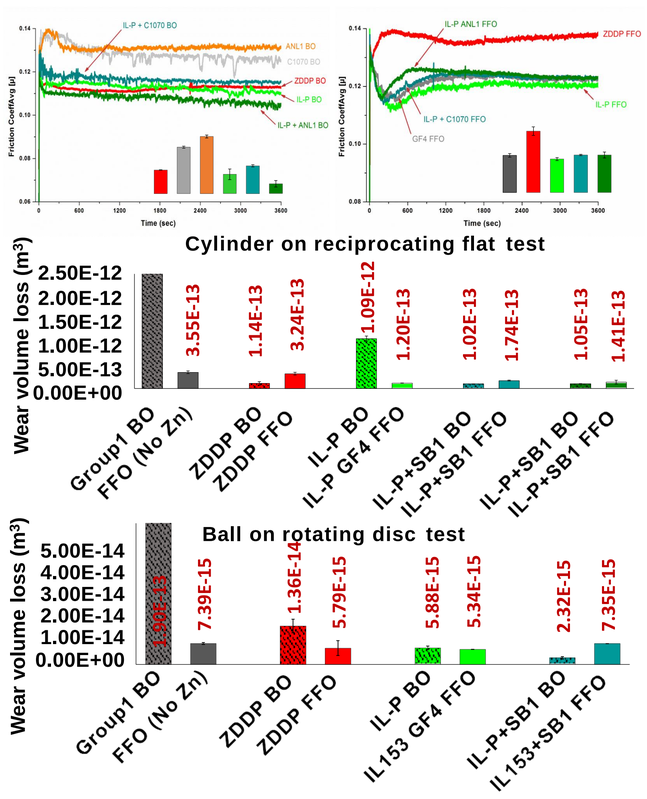
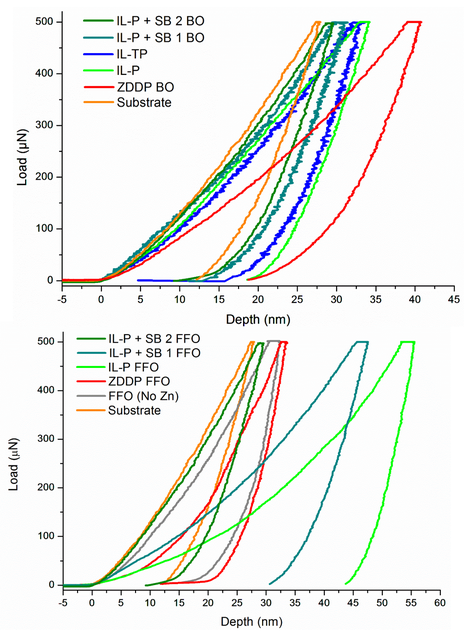
Introduction

Synergistic interaction between ionic liquid (IL) and soluble boron additives were studied for anti-wear application. Ionic liquids composed of phosphonium cation and phosphate anion (IL-P) was mixed with soluble boron additives in group I base oil as well as in GF4 grade fully formulated oil (no zinc & no phosphorus). Base oil formulations were prepared keeping the phosphorous level at 1000 ppm and GF4 grade fully formulated oil formulations were prepared keeping the phosphorous level at 700 ppm. Anti-wear performance of the mixtures obtained was evaluated using a cylinder on reciprocating flat and a ball on rotating disc contact. Friction and wear properties were compared with those of a reference oil containing ZDDP.

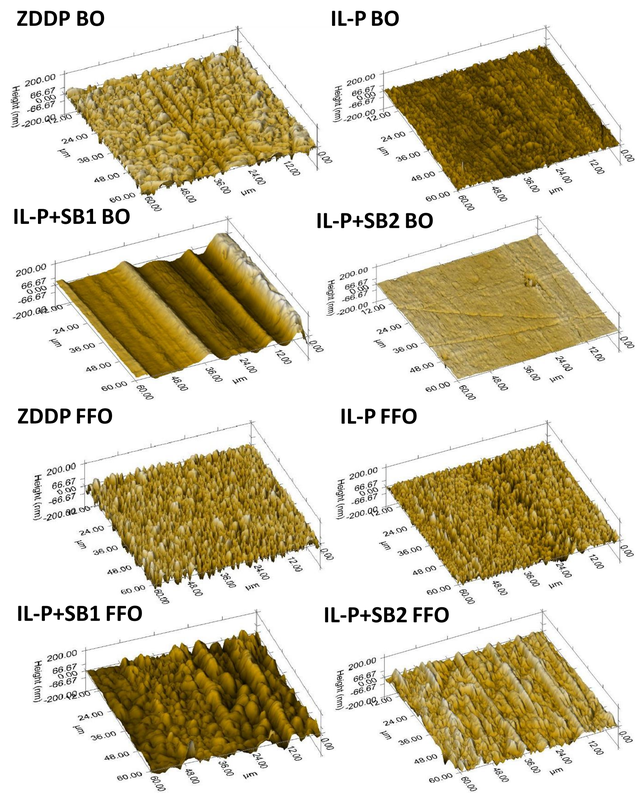
Friction and wear analysis



Nano-mechanical property of tribofilms

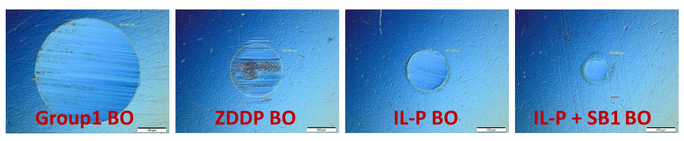


SPM imaging: topography of rubbed surfaces



Objectives

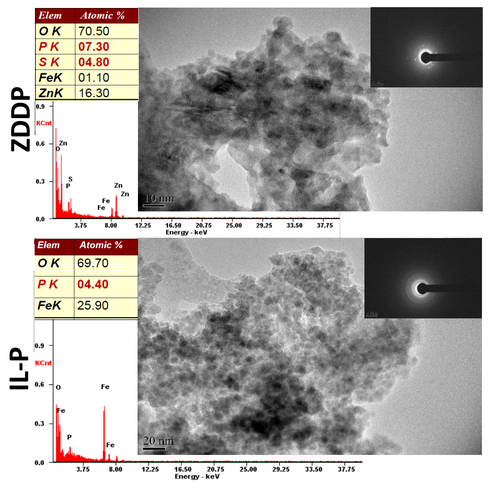
- Develop an understanding on the mechanism of tribofilm formation using binary additive mixture of phosphonium ILs with soluble boron chemistry as lubricant additive in group I base oil as well as in fully formulated oil (no Zn & no P).
- Study and understand the synergism between phosphonium ILs and soluble boron additives.
- Scale the tribological performance of these novel additive mixture with ZDDP.
- Characterization of chemical and mechanical properties of tribofilms and develop an understanding between the tribofilm properties with their respective tribological behaviour.



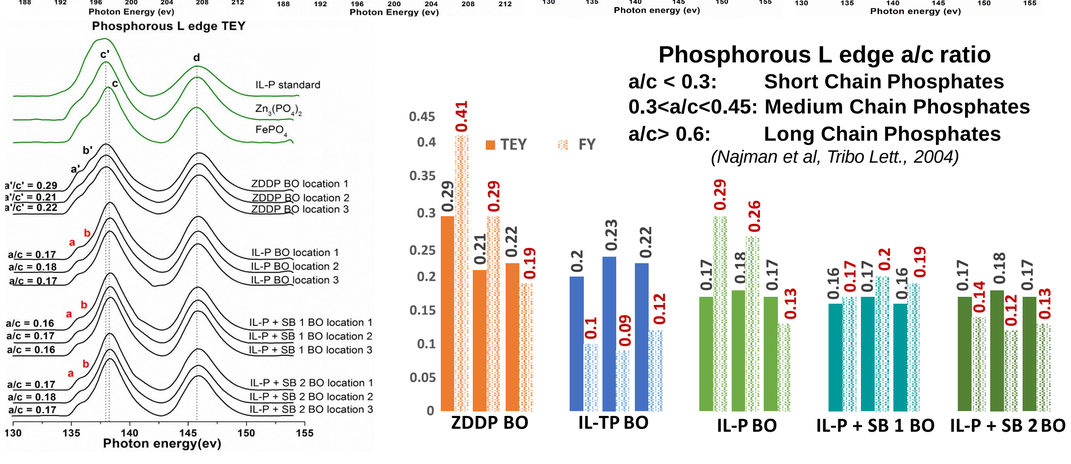
IL-P & IL-P+SB tribofilms show lower penetration in comparison to ZDDP tribofilms in base oil formulations. In case of FFO, tribofilms show wide penetration range. SPM images show addition of boron additives to IL-P results in much smoother wear track.

In comparison with ZDDP no significant improvement in CoF of IL-P & IL-P+SB in BO. In case of FFO, ZDDP shows relatively higher CoF. Addition of SB to IL-P shows improvement in anti-wear behaviour. Wear losses are similar or even lower than ZDDP are observed.

Tribological test	Load Applied, Lubricating Oil, Tribofilms	Ball, Wear track, Vertical load applied, Direction of rotation, Disc
Oil matrix	Group I mineral base oil	GF4 grade fully formulated oil (No Zn, No P)
Viscosity	10.068 mm²/sec at 100 °C	10.02 mm²/sec at 100 °C
Treat rate	**Phosphorous: 1000 ppm (BO), 700 (FFO) & Boron: 200 ppm**	**Phosphorous: 1000 ppm (BO), 700 (FFO) & Boron: 200 ppm**
Applied load	82 N (p_{max} = 500 MPa)	2 N (p_{max} = 510 MPa)
Temperature	100 °C	100 °C
Speed	0.06 m/sec, 5 Hz	0.06 m/sec
Stroke length	6 mm	
Cylinder/Ball	Φ 4 mm x 6 mm, 52100 steel (61 HRc)	Φ 12.7 mm, 52100 alloy steel
Flat/Disc	12 mm x 12 mm x 8 mm, 52100 alloy steel (61 HRc)	Φ 20 mm, 52100 alloy steel
Duration	1hr	1hr



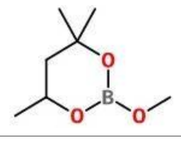
BF TEM image of ZDDP wear debris shows mostly amorphous particles of zinc polyphosphates (EDX) and few crystallites mainly oxides of iron as well as zinc sulfates/sulfides. BF image of IL-P wear debris shows crystallite species mainly of iron oxide and iron polyphosphates (EDX)



Phosphorous L edge a/c ratio

a/c < 0.3: Short Chain Phosphates
0.3<a/c<0.45: Medium Chain Phosphates
a/c> 0.6: Long Chain Phosphates
(Najman et al, Tribo Lett., 2004)

Boron is primarily present in the form of boric acid/boron oxide (peak 'a' in Boron K edge FY BO and FFO) and to some extent boron phosphate (peak 'b') in the tribofilms formed using SB and IL-P+SB. In case of BO, Phosphorous is primarily present as zinc polyphosphates (ZDDP tribofilms) and iron polyphosphates (IL-P & IL-P+SB tribofilms). The P-Ledge pre-edge (peak a/a') to absorption edge (peak c/c') ratio suggests that tribofilms are mainly composed of short chain polyphosphates where ZDDP tribofilms show relatively higher chain length and IL-P+SB tribofilms show more consistent chain length at three different locations as well as in TEY (up to 10 nm) and FY (up to 60 nm) mode. In case of FFO, P-Ledge shows that tribofilms are primarily composed of short chain tri-calcium phosphates irrespective of antiwear chemistry used.

Code	Chemical name	Chemical formula
ZDDP	Zinc Dialkyl Dithiophosphate	 R = 1°, 2°, 3° alkyl or aryl group
IL-P	Trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate	
SB 1	2-Methoxy-4,4,6-trimethyl-1,3,2-dioxaborinane	
SB 2	ANL1	Proprietary at this point

Conclusions

- Binary additive mixtures of IL-P and SB show similar or even better antiwear performance in comparison to ZDDP.
- 3D wear profile using SPM technique shows much smoother wear surfaces resulted from IL-P+SB lubrication. Force displacement data show lower penetration range of IL-P & IL-P+SB tribofilms in comparison to ZDDP tribofilms for BO formulations.
- XANES study of tribofilms shows tribofilms are primarily composed of boric acid/boron oxide, boron phosphate (some extent) and short chain poly phosphates of Zn and Fe (ZDDP BO and IL-P BO & IL-P+SB BO) and tri-calcium phosphate (FFO).

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