SUPPLEMENTARY MATERIAL FOR THE PAPER

Tribochemistry of Triphenyl Phosphorothionate (TPPT) by *In Situ* Attenuated Total Reflection (ATR/FT-IR) Tribometry

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Short Title: *Tribochemistry of TPPT on Air-oxidized Iron: an In Situ ATR/FT-IR Investigation*

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This document contains the supplementary material for the paper "Tribochemistry of Triphenyl Phosphorothionate (TPPT) by *In Situ* Attenuated Total Reflection (ATR/FT-IR) Tribometry".

Section 1 contains supporting experimental details.

Table S.1 lists the transmission FT-IR and ATR/FT-IR experimental conditions.

Table S.2 lists the peak-fitting parameters for the high-resolution XP-spectra (data acquired in standard lens mode, *Std*) of iron-coated germanium ATR crystal after tribological testing at 423 K for 18 hrs in the presence of a 0.044 mol dm^{-3} solution of TPPT in PAO.

Figure S.1 shows the transmission FT-IR spectrum of purified TPPT. The IR peaks and assigned functional groups are listed in Table S.3.

Section 1

S.1 Experimental

S.1.1 Tribological Testing

The tribopair employed in the present work consisted of an iron-coated (10 nm) germanium ATR crystal and of a fixed 18Cr10Ni steel cylinder. In order to further reduce the surface roughness of the steel cylinder and to ensure a line contact between the cylinder and the crystal surface, the cylinders were pre-conditioned using the ATR/FT-IR tribometer and sweeping them back and forth along a 18Cr10Ni steel bar (having the same dimensions of the ATR crystal and mounted in an ATR crystal holder), on top of which either emery paper (P1200 and P2400) or polishing cloths were fixed. After the last polishing step, performed using a 3 μm diamond paste, the cylinder was ultrasonically cleaned in ethanol (puriss p.a., Fluka, Buchs, Switzerland). Such a preparation procedure resulted in the presence of a small worn area at the bottom of the cylinder, whose width was 23±3 μm. The root-mean-square roughness (R_q, defined according to ISO 4287:1997) of the as-received cylinder was 682±147 nm, while that of the worn area produced on the cylinder following grinding and polishing was 187±51 nm.

The tribological tests were carried out by pouring ca. 1.5 cm^3 of oil solution onto the iron-coated germanium ATR crystal and then heating the assembly to the desired temperature, i.e. 423 K. Once the desired temperature was reached (in ca. 40 min), the tribological experiment was started. In the present work, a normal load of 6.9 N (corresponding to an average contact pressure of 57±10 MPa), a sliding speed of 0.5 mm/s and a stroke of 45 mm were used. During the experiments the solution was open to air. The relative humidity (RH) was between 20 and 40 %.

ATR/FT-IR spectra were collected at 298-303 K both before and during tribological testing. Cooling the system to 298-303 K after stopping the tribotest and before the acquisition of ATR/FT-IR spectra was necessary due to the strong reduction in the transmittance of the germanium ATR element at elevated temperatures. As pointed out by Piras [1, 2], germanium becomes opaque at wavenumbers below 1600 cm^{-1} at 423 K. This effect is even more pronounced when

the crystal is coated with iron: the transmittance of the iron-coated germanium crystal is almost zero over the whole spectral range at 423 K.

S.1.1.1 Data Processing

The frictional data were processed using the time-averaging data reduction method reported in [3]. In order to avoid end-point effects, i.e. variation of the frictional data at the positions where the sliding direction changes, only the data points corresponding to a slider (or cylinder) position between 1/6 and 5/6 of the stroke length were considered for calculating the average coefficient of friction (CoF) and its standard deviation over one sliding cycle (one cycle equals two stroke lengths [4]).

S.1.2 Fourier-transform Infrared Spectroscopy (FT-IR)

S.1.2.1 Data Processing

The FT-IR spectra were processed with OMNIC™ software (V7.2, Thermo Electron Corporation, Madison, WI, USA).

In the case of the transmission FT-IR spectra, a single-beam spectrum of the KBr pellet was acquired before each measurement as a background. Normalization with respect to the methyl asymmetric deformation band, overlapped by the methylene scissor vibration band, of PAO at 1466 cm^{-1} [5] was performed.

As for the ATR/FT-IR spectra, a background correction was always applied to the experimental spectra using the single-beam spectrum of the iron-coated germanium ATR crystal collected before each experiment. All the ATR/FT-IR spectra presented in this work are reported without any baseline or ATR correction.

Table S.1. Transmission FT-IR and ATR/FT-IR experimental conditions

	Transmission FT-IR	*ATR/FT-IR*
Detector	DTGS	MCT/A
Beamsplitter	KBr	KBr
Spectral Range (cm^{-1})	4000-400	4000-600
Resolution (cm^{-1})	2	4
Number of Scans	64	1024
Scan Velocity (cm/s)	0.6329	2.5317
Acquisition Time (s)	136	568
Gain Control	1	1

Table S.2. Peak-fitting parameters for the XP-spectra of a Ge ATR crystal coated with iron (10 nm) tribostressed at 423 K for 18 hrs in the presence of a 0.044 mol dm^{-3} (1.82 wt.%) solution of TPPT in PAO. The uncertainty of the binding energies (BE) and of the full width at half-maximum (FWHM) is 0.1 eV

Element	*Assignment*	*BE (eV)*	*FWHM (eV)*
C 1s	C-C	285.0	1.5
	C-O-CO /**C**-O-P	286.3	1.5
	C-**C**O-C	287.6	1.5
	CO_3/**C**OOX	289.2	1.5
O 1s	Fe Oxide	530.1	1.6
	PO_4^{3-}/NBO/SO_4^{2-}	531.7	1.6
	C**O**$_3$/-C**O**-O-/ C-C**O**-C/Ge Oxide	532.4	1.6
	-CO-**O**-/BO/C-**O**-P	533.5	1.6
	Ox. Org. Comp.	534.7	1.6
Fe 2p$_{3/2}$	deg./Fe carbonate/Fe Oxide	709.9	1.8
	Fe(II) phosphate	712.1	2.4
	Fe(III) phosphate/sulphate	714.1	2.4
	deg. sat.	715.4	1.8
	Fe(II) phosphate sat.	717.6	2.2
P 2p$_{3/2}$	PO_4^{3-}/ $P_2O_7^{4-}$	133.7	1.5
	Polyphosphates (long chain)	135.0	1.5
S 2p$_{3/2}$	SO_4^{2-}	168.9	1.4
	Sulfoxides	170.0	1.4
Ge 2p$_{3/2}$	Ge Oxide	1221.1	2.1

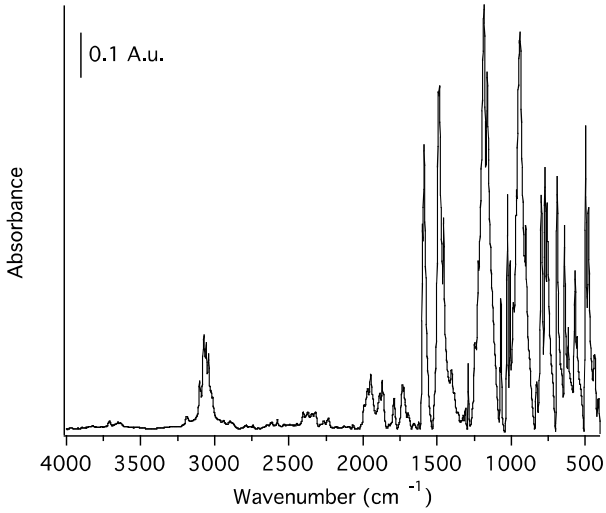

Figure S.1. Transmission FT-IR of purified TPPT. Three spectral regions can be distinguished: i) 3150-3000 cm^{-1}: aromatic CH stretching vibrations, ii) 2100-1660 cm^{-1}: overtone and combination bands due to the CH out-of-plane deformation vibrations, iii) 1600-400 cm^{-1}: fingerprint region [6]

Table S.3. IR frequencies (cm^{-1}) and functional groups for the transmission FT-IR spectrum of purified TPPT [6]

Frequency (cm^{-1})	*Functional Group*
3102 w, 3095, 3072, 3057, 3040, 3025 s, 3013 w	νCH
2067, 1992, 1967,1947, 1884, 1869, 1790, 1734, 1723, 1696	Overtone and combination bands due to γCH
1598, 1587 s, 1490, 1483 s	νPh
1455	ωP-O-Ar
1289, 1245, 1221	δCH
1183 vs, 1161	νC-O-(P)
1074, 1068, 1024	δCH
1007	νPh
984 w, 963 w	γCH
940 vs	νP-O-(C)
900, 830, 825	γCH
796 m	P=S (I)
771 m, 758	ν_sP-O-(C)
690	γCH
639 m	P=S (II)
614	δCH
573, 568, 555 w	δP-O-Ar
497, 479	γCH

ν: stretching; γ: out-of-plane deformation vibration; δ: in-plane deformation vibration; ω: wagging

References

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