

SOME ASPECTS OF OIL LUBRICANT ADDITIVATION WITH ZnO NANOPARTICLES

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SYNOPSIS

This is a study on the tribological behaviour of ZnO nanoparticles as an additive in a polyalphaolefin (PAO6) and on the influence of dispersing agents (OL100 and OL300). Anti-wear and extreme pressure tests were run on two four-ball machines. Firstly, it was demonstrated that OL300 has better dispersant properties than OL100, and also was found formation of aggregates for 1 and 1.5% of ZnO in PAO6 + 3% OL300 suspension. Ensuing SEM and EDS analysis of the worn surface highlighted a number of conclusions: OL100 and OL300 are potentially useful as wear reducer additives in PAO6, the non-coated ZnO nanoparticles had an abrasive behaviour, and ZnO nanoparticles do not act as anti-wear agent under certain conditions but in EP conditions they can decrease wear.

INTRODUCTION

Friction and surface damage in machines and industrial gears caused by extreme operation conditions can be reduced by applying extreme pressure (EP) and anti-wear (AW) additives to lubricants. These additives tend to be sulphur-, chlorine- and phosphorous-containing compounds. As an environmental protection measure, the use of chlorine- and phosphorus-containing compounds used as lubricant additives has been restricted, and so developing new additives that pollute less has therefore become the target for researchers (Huang and et.al., 2002).

The tribological properties of graphite, polytetrafluoroethylene (PTFE), MoS₂, TiO₂, La(OH)₃, PbS, LaF₃, lanthanum borate, titanium borate, zinc borate, ferric oxide, ferrous borate, Ni and CaCO₃ nanoparticles used as oil additives have all been investigated (Hernández, 2005). Results show that they can deposit on the rubbing surface and improve the tribological properties of the base oil, while it has been reported that micron particles of a certain hardness would result in abrasive friction.

The objective of this paper is to study the tribological behaviour of ZnO nanoparticles as an additive in a polyalphaolefin (PAO6) and on the influence of the used dispersing agents.

EXPERIMENTAL DETAILS

The main properties of the nanoparticles, lubricant and dispersing agents used are listed in Table 1. ZnO nanoparticles with 20 nm in size were first manually dispersed in the dispersing agent, and suspensions in PAO6 were prepared by adding the nanoparticle-dispersing agent mixtures to PAO6 and stirring in an ultrasonic probe for 2 min. Dispersing agents and nanoparticle concentrations were 1–1.5–3 and 0.3–1–3 wt.%, respectively.

Table 1. Material properties

<i>Materials</i>	<i>Properties</i>
Nanoparticles	
ZnO	Morphology: nearly spherical, Purity: 99.5%, Size: 20 nm
Lubricant	Physical properties
PAO6	Density (15.6°C): 0.826 g/cm ³ Viscosity: 31.0 cSt (40°C) 5.90 cSt (100°C) VI: 135
Dispersing agents	Description
OL100	Commercial name: Octacare (R) DSP-OL100 Density: 0.91 g/cm ³ Character: non-ionic
OL300	Commercial name: Octacare (R) DSP-OL300 Density: 0.90 g/cm ³ Character: non-ionic
Test balls	Chemical composition
AISI 52100	0.98-1.1%C, 0.15-0.30%Si, 0.25-0.45%Mn, 1.30-1.60%Cr, <0.025%P, <0.025%S

All test-section components were cleaned ultrasonically with heptane for 10 min and dried with hot air before and after tests. Wear tests were then carried out on a Falex Roxana four-ball machine in line with the ASTM D4172 standard (speed: 1200 rpm, load: 392 N, time: 60 min, temperature: 75°C). The test machine used for extreme pressure tests (ASTM D2783) was a Stanhope Seta Shell Four-Ball EP Lubricant Tester with a driving shaft speed of 1470 rpm. The 12.7 mm. diameter test balls with a roughness of $R_a = 0.035 \mu\text{m}$ used in this study were made from AISI 52100 steel with a hardness of 65 RC (Table 1). Wear scar diameters (WSD) were measured using a Nikon PFX optical microscope, provided with a Nikon F-301 CCD camera. The following parameters were obtained from the extreme pressure tests: initial seizure load (ISL), weld load (WL) and load wear index (LWI).

The topography of the wear scar surface was studied by scanning electron microscopy (SEM JEOL-6100); energy dispersive spectrometry (EDS) was used to detect the elements present on wear scar surfaces.

RESULTS

Both OL300 and OL100 acted as anti-wear agent when they were added to PAO6, although the former outperforms the latter. Fig. 1 highlights that the influence of both OL100 and OL300 concentrations of between 1 and 3% was negligible on WSD. Elemental analysis showed that the dispersing agents did not chemically interact with the metallic surface.

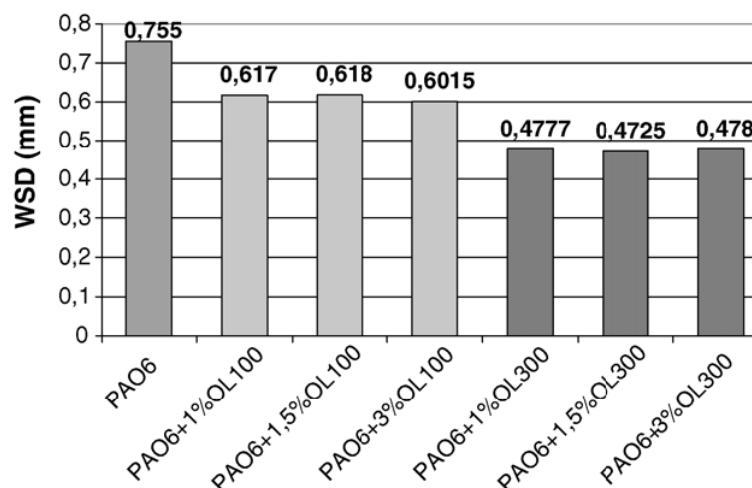


Fig. 1. Results of anti-wear tests using PAO6 and the binary mixtures PAO6 + OL100 and PAO6 + OL300.

OL300 not only outperformed OL100 as an AW agent, but also proved to be a better dispersing agent of ZnO nanoparticles in PAO6. A stability study was carried out by sedimentation with results showing that aggregates and flocs were formed at all OL100 concentrations. Fig. 2 shows the AW properties of a number of PAO6 + OL300 + ZnO suspensions compared to PAO6 and PAO6 + OL300. Wear scar diameters using these mixtures were smaller than those obtained with background oil (PAO6). However, when 0.3% ZnO nanoparticles was added to PAO6 + 1% OL300 and PAO6 + 1.5% OL300 mixtures, WSD was higher than for these mixtures. In contrast, adding 0.3% of ZnO in PAO6 + 3% OL300 failed to change the WSD.

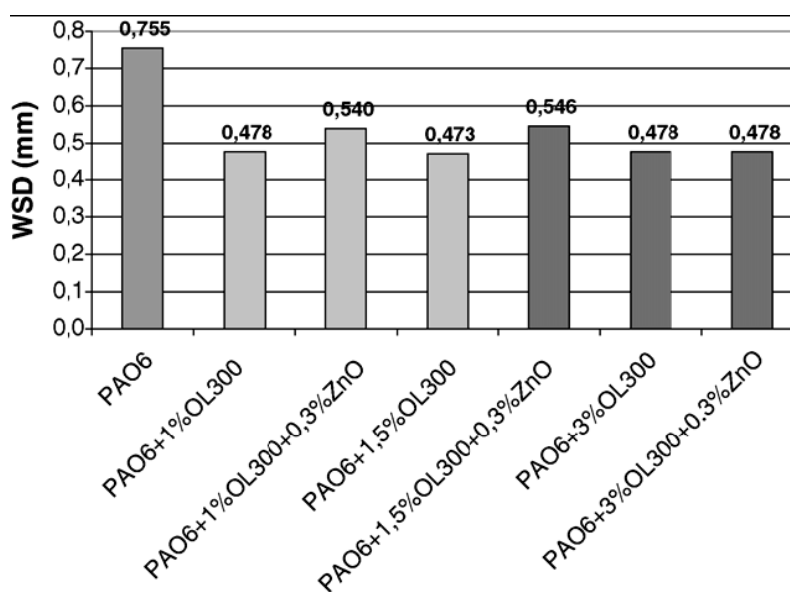


Fig. 2. Results of anti-wear tests of PAO6 + OL300 + ZnO suspensions.

A stability study also showed formation of aggregates for PAO6 + 1% OL300 and PAO6 + 1.5% OL300 mixtures, so this wear behaviour may be explained by not all the nanoparticles being coated by 1 and 1.5% of OL300 and therefore colliding and sticking to form larger particles, which act as abrasive bodies, Fig. 3. The abrasive behaviour of non-coated ZnO

nanoparticles was observed in a wear test without dispersing agents, Fig. 4. In this case, with a WSD of 0.817 mm, which is a higher value than the 0.755 for pure PAO6, Zn was not found on the wear scar surface.

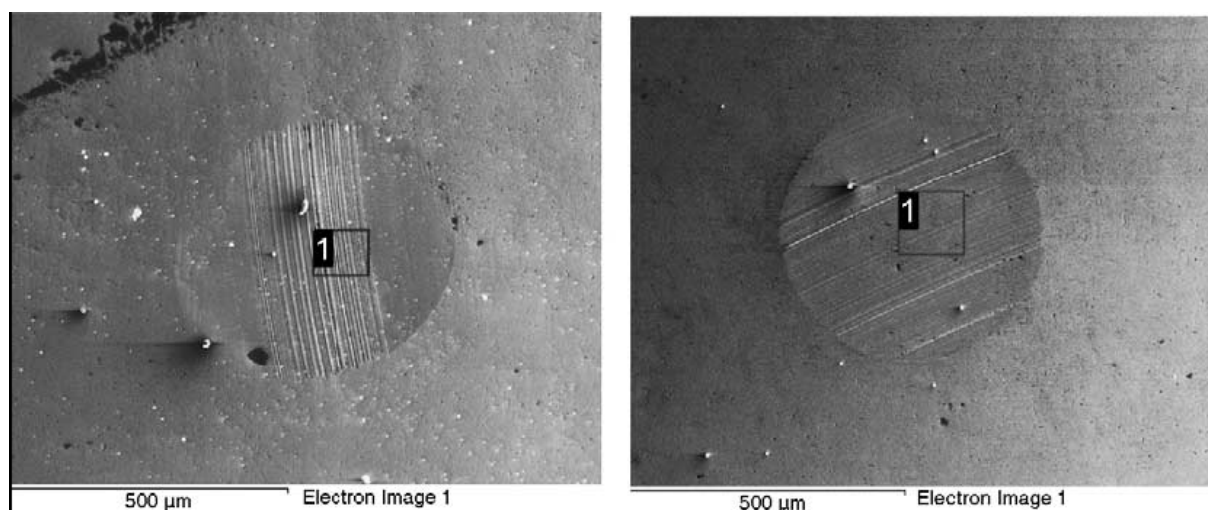


Fig. 3. Micrographs ($\times 100$, scale: 500 μm) after anti-wear tests:
Left panel: PAO6 + 1% OL300 + 0.3% ZnO; right panel: PAO6 + 3% OL300 + 0.3% ZnO.

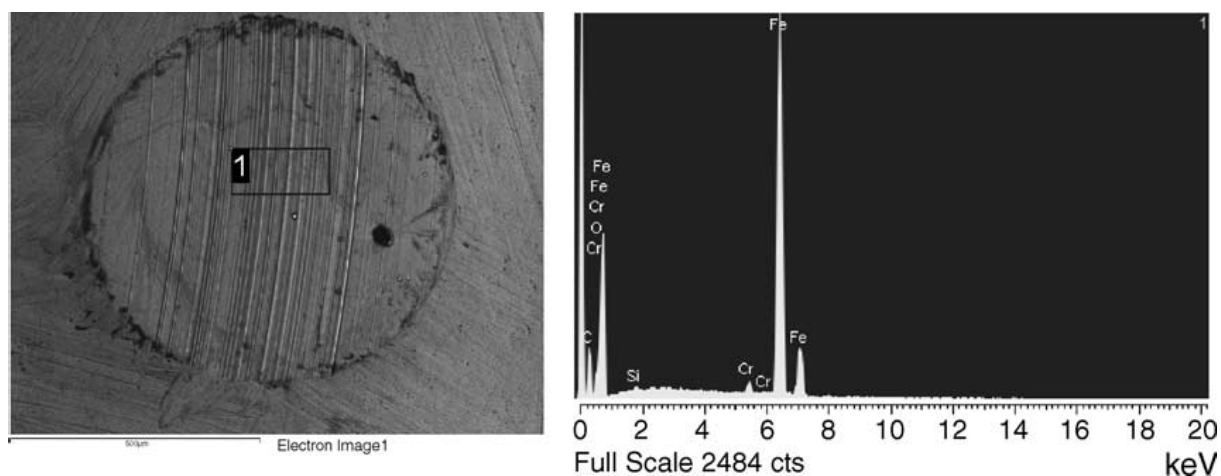


Fig. 4. Micrograph ($\times 100$, scale: 500 μm) and EDS of wear scar using PAO6 + 0.3% ZnO (ASTM D4172).

The lower hardness of ZnO (HRC 32) compared to the steel surface (HRC 65) was verified by using the Mohs scale, which was then converted into its Rockwell C equivalent. Thus, as Wan and Spikes (1987) reported, large suspended particles of lower nominal hardness than bearing steel do indeed damage steel surfaces. Nikas (2001a, 2001b, 1999) and Sayles and Ioannides (1988) have also reported that soft/ductile particles can cause damage of equivalent severity as hard particles. This phenomenon occurs because plastically compressed soft/ductile particles in an EHD contact are flattened and offer a much larger interface for friction, as opposed to hard particles, which more or less retain their initial shape. In short, given the prevalence of thermal stress over mechanical stress, soft particles can cause damage of equivalent severity as hard particles (Nikas, 2001b).

Anti-wear test results of suspensions with 0.3–3 wt.% ZnO in PAO6 + 1% OL300 and PAO6 + 3% OL300 are shown in Fig. 5. All PAO6 + 1% OL300 + ZnO suspensions displayed worse wear behaviour than PAO6 + 1% OL300 alone. Increasing the ZnO concentration hardly affected the WSD in practical terms. WSD rose for PAO6 + 3% OL300 when the ZnO concentration was above 0.3 wt.%, most likely due to non-coated nanoparticles in the suspension. Higher ZnO concentrations were seen not only to increase the abrasive component but also to cause Zn deposition on the ball surface, as shown in Fig. 6.

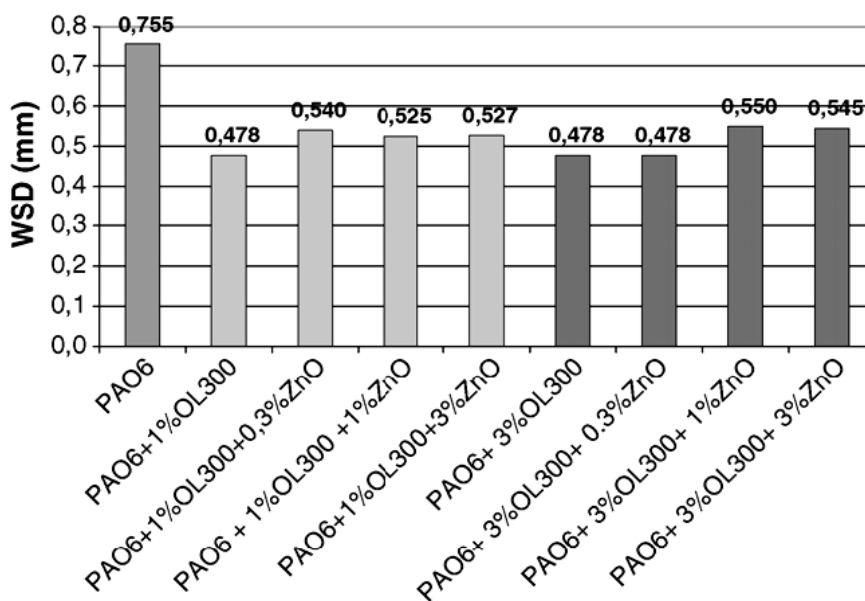


Fig. 5. Influence of the ZnO concentration in anti-wear properties of PAO6 + OL300 + ZnO suspension.

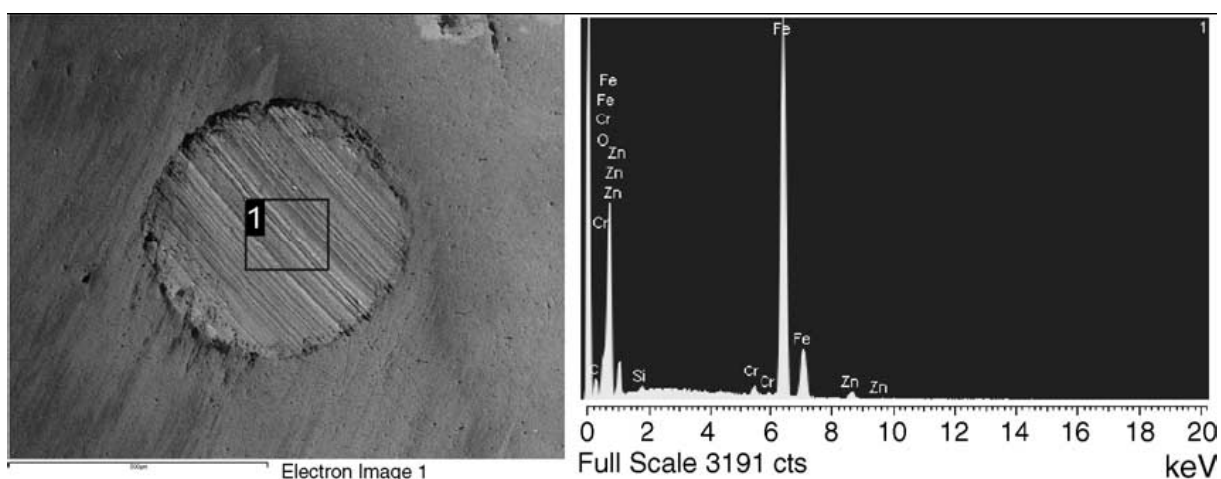


Fig. 6. Micrograph ($\times 100$, scale: 500 μm) and elemental analysis of wear scar with PAO6 + 1% OL300 + 3% ZnO (ASTM D4172).

These results justify our claim that ZnO nanoparticles do not work as an anti-wear agent. If nanoparticles are not coated by dispersing agents, wear can even increase. However, in EP conditions, from the initial seizure load, ZnO nanoparticles decreased wear, Figs. 7-8. Table 2

demonstrates how greater ZnO concentration in a PAO6 + 1% OL300 mixture decreases the WSD at initial seizure load (ISL) and before weld load, and consequently increases the LWI. However, in the PAO6 + 3% OL300 mixture, 0.3% ZnO provided the best EP behaviour.

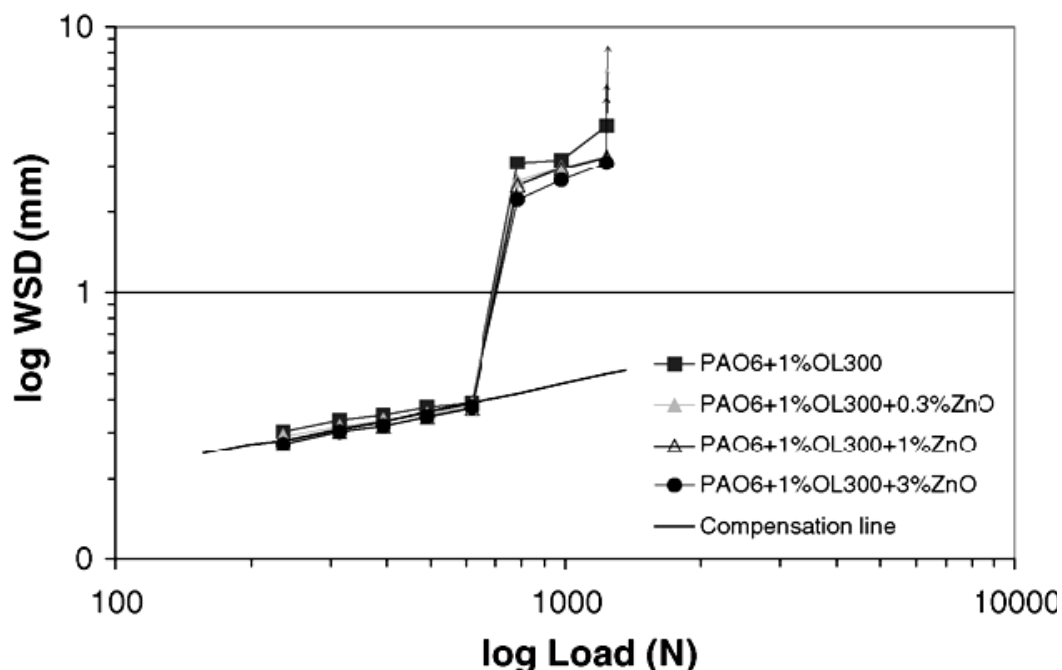


Fig. 7. Log load vs. log wear scar diameter of PAO6 + 1% OL300 + ZnO suspensions.

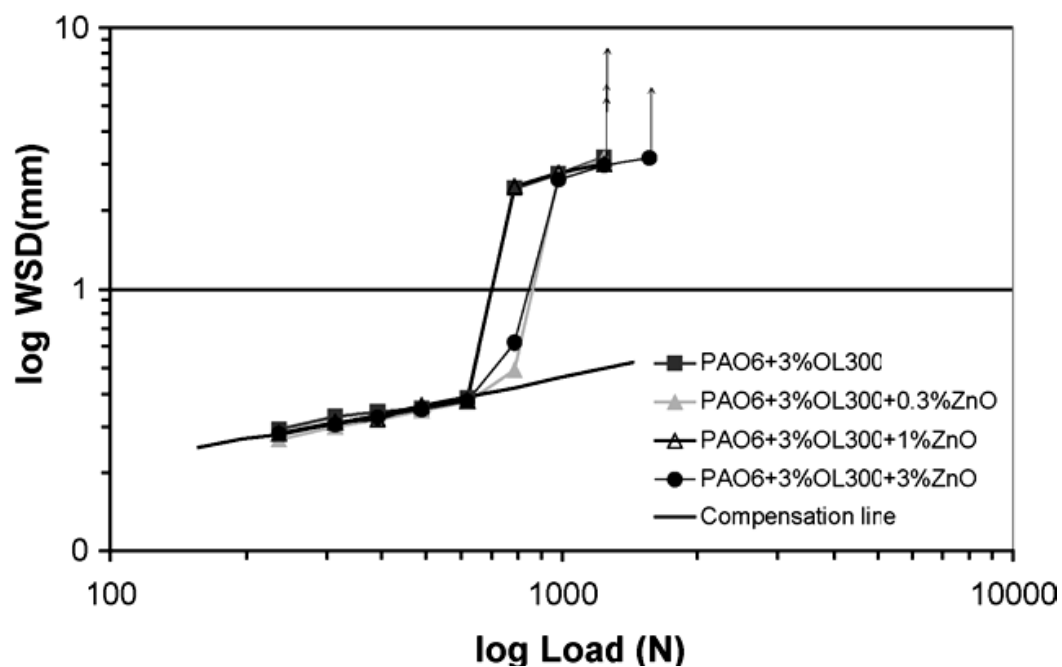


Fig. 8. Log load vs. log wear scar diameter of PAO6 + 3% OL300 + ZnO suspensions.

Table 2 Extreme pressure properties.

Lubricant	Initial seizure load, ISL (N)	Mean wear scar diameter at ISL (mm)	Weld load, WL (N)	Mean wear scar diameter at just before weld load, JBWL (mm)	Load Wear Index, LWI (N)
A	784.8	3.084	1569.6	4.259	242.03
B	784.8	2.611	1569.6	3.274	255.92
C	784.8	2.521	1569.6	3.233	263.86
D	784.8	2.226	1569.6	3.077	267.32
E	784.8	2.424	1569.6	3.184	256.26
F	784.8	0.492	1569.6	3.144	313.77
G	784.8	2.469	1569.6	3.000	261.04
H	784.8	0.622	1962.0	3.162	309.84

A: PAO6+1%OL300

B: PAO6+1%OL300+0.3%ZnO

C: PAO6+1%OL300+1%ZnO

D: PAO6+1%OL300+3%ZnO

E: PAO6+3%OL300

F: PAO6+3%OL300+0.3%ZnO

G: PAO6+3%OL300+1%ZnO

H: PAO6+3%OL300+3%ZnO

The enhanced EP behaviour of the suspensions was related to enhanced ZnO nanoparticle concentration and their deposition on wear scar surface. As not all nanoparticles are coated by dispersing agent in the PAO6 + 1% OL300 mixture, elemental analysis showed the appearance of Zn on the wear scar surface at ISL, Fig. 9; therefore, the higher the percentage of ZnO in the mixture, the higher the amount of Zn on the surface, Fig. 10.

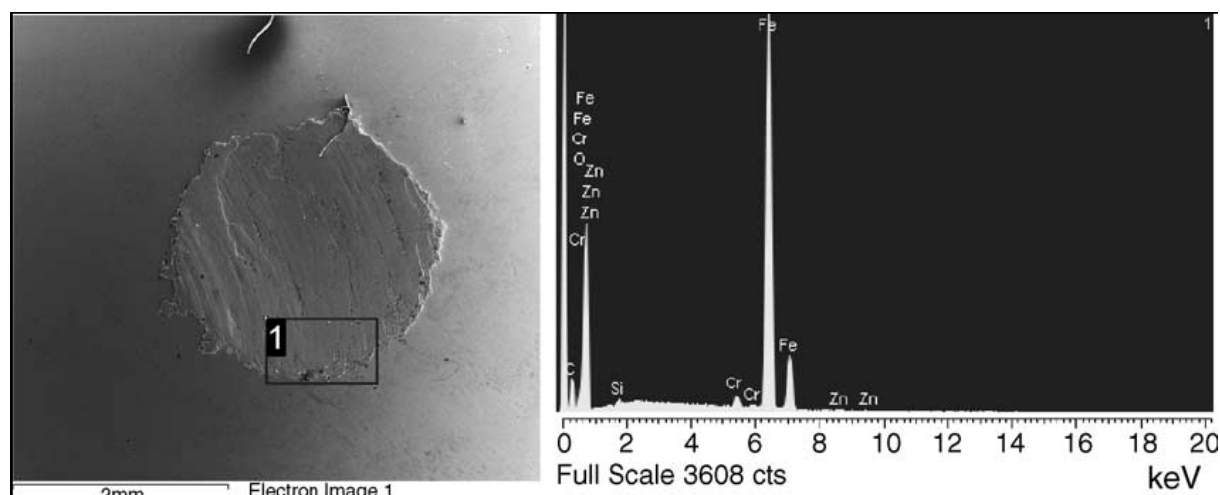


Fig. 9. Micrograph ($\times 20$, scale: 2 mm) and elemental analysis of PAO6 + 1% OL300 + 1% ZnO at initial seizure load.

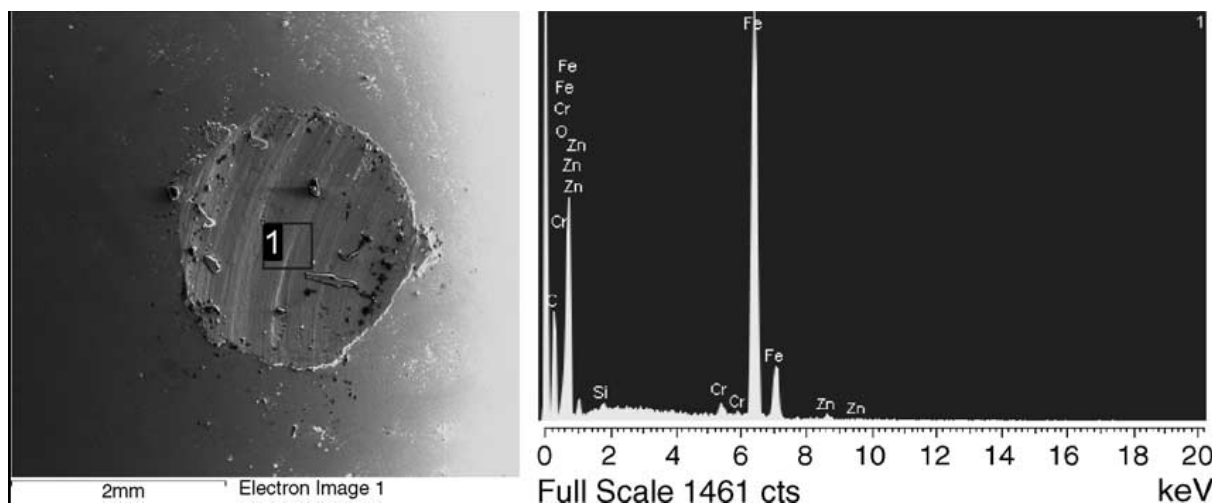


Fig. 10. Micrograph ($\times 20$, scale: 2 mm) and elemental analysis of PAO6 + 1% OL300 + 3% ZnO at initial seizure load.

For PAO6 + 3% OL300 mixture, the best EP behaviour, Table 2, was provided by 0.3% of ZnO, when Zn did not appear on the wear scar surface at ISL, Fig. 11. This result could be also related to the fact that 3% of OL300 coat all nanoparticles.

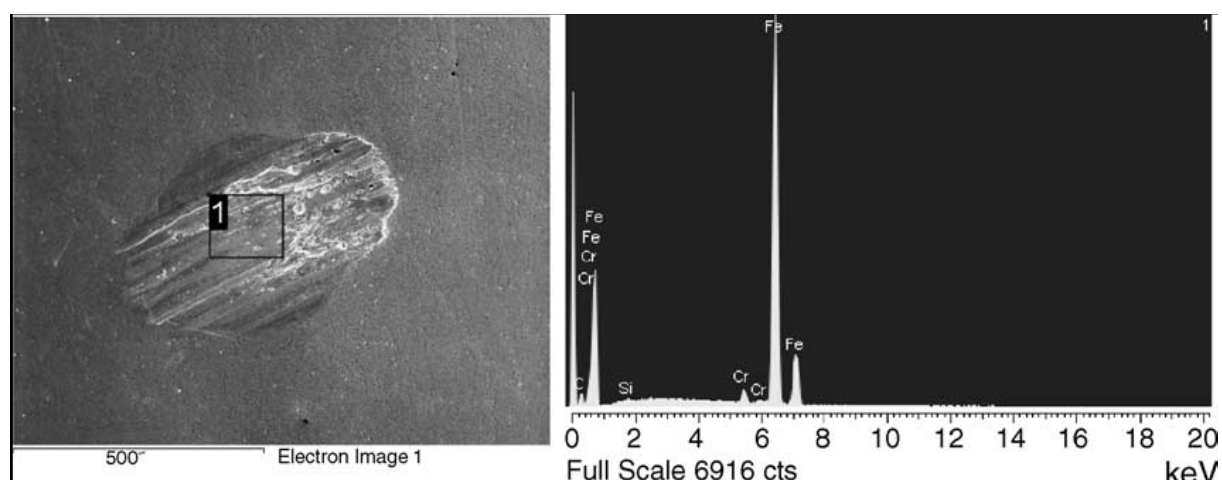


Fig. 11. Micrograph ($\times 100$, scale: 500 μm) and elemental analysis of PAO6 + 3% OL300 + 0.3% ZnO at initial seizure load.

CONCLUSIONS

Both esters (OL100 and OL300) showed their potential as wear reducer additives in PAO6, but OL300 had a better behaviour as dispersing agent of ZnO nanoparticles in PAO6. The stability study shows formation of aggregates for 1 and 1.5% of ZnO in PAO6 + 3%OL300 suspension, and these non-coated ZnO nanoparticles displayed an abrasive behaviour in the AW region, independently of its lower hardness compared to steel surfaces. ZnO nanoparticles do not function as an anti-wear agent under certain conditions; however, in EP conditions they can decrease wear, even without Zn deposition.

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