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Comparison Between the Action of Nano-Oxides and Conventional EP Additives in Boundary Lubrication

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Abstract: Additives are essential in lubricant development, improving their performance by the formation of a protective film, thus reducing friction and wear. Some such additives are extreme pressure additives. However, due to environmental issues, their use has been questioned because their composition includes sulfur, chlorine, and phosphorus. Nanoparticles have been demonstrated to be a suitable substitute for those additives. This paper aims to make a comparison of the tribological performance of conventional EP additives and oxides nanoparticles (copper and zinc) under boundary lubrication conditions. The additives (nanoparticles, ZDDP, and sulfur) were added to mineral and synthetic oils. The lubricant tribological properties were analyzed in the tribometer HFRR (high frequency reciprocating rig), and during the test, the friction coefficient and percentual of film formation were measured. The wear was analyzed by scanning electron microscopy. The results showed that the conventional EP additives have a good performance owing to their anti-wear and small friction coefficient in both lubricant bases. The oxides nanoparticles, when used as additives, can reduce the friction more effectively than conventional additives, and displayed similar behavior to the extreme pressure additives. Thus, the oxide nanoparticles are more environmentally suitable, and they can replace EP additives adapting the lubricant to current environmental requirements.

Keywords: boundary lubrication; EP additives; oxides nanoparticles

1. Introduction

A good lubricant is selected according to its ability to form a protective film on sliding parts, resist high temperatures, and support mechanical loads. In order to improve lubricant performance characteristics, it is necessary to use additives. The most commonly used additives are antioxidants and extreme pressure agents (EP) to act in boundary lubrication conditions. These EP additives prevent high wear caused by contact between metal to metal under high loads. The wear and friction performance at the boundary lubrication regime is controlled mainly by the lubricant additives, which form films on surfaces or create a layer of the sacrificial film [1]. This film formation depends on the nature and chemistry of additives added to the lubricant oil. However, these additives remain subject some restrictions on their use due to their environmental impacts [2,3].

Some traditional EP additives are ZDDP (zinc dialkyl dithiophosphate) and compounds with sulfur. For lubricants containing ZDDP anti-wear additives, such rubbing has been shown to induce the formation of thick tribofilms that protect the moving surfaces against wear [4,5]. ZDDP is still used in the majority of commercial lubricants, despite considerable efforts in the last two decades to replace them with alternative anti-wear additives, since the presence of sulfur and phosphorus oxides and metal salts in ZDDP is harmful [6]. However, the adverse results of this additive were reported when the speed is increased [7,8]. Thus, in applications where speed is a parameter that changes, it is necessary to incorporate other additives.

The sulfur and phosphorus-based additives withstand high loads reacting quickly with the free atoms on the surface, forming sulfides and phosphides [9]. Furthermore, the chlorine compounds react only at high temperatures avoiding the welding in the high points of the surface [1]. The use of sulfur, phosphorus, and chlorine as additives in lubricants are used because they increase the lifetime of machines [10,11].

Over the past decade, many studies have been carried out on applications of nanoparticles in the field of lubrication. Therefore, the addition of nanoparticles to conventional lubricants can significantly promote the reduction of friction and wear [1,3,12–25]. However, dispersing them in oils has been a challenge because metal oxide nanoparticles easily agglomerate due to their high surface tension [20].

In lubricants, oxides nanoparticles are deposited on the surface to form a thin film that prevents contact between the surfaces. This layer improves the tribological properties of the lubricating oil, reducing the friction and wear as well as improving the load-carrying capacity, even at low concentrations [14–16,26]. Few works have investigated the performance of nanoparticles associated with conventional EP additives. Aldana et al. [27] compared WS_2 nanoparticles with ZDDP additive, obtaining a better tribological performance when the nanoparticles were used in the presence of ZDDP. A substantial reduction of the friction coefficient was observed, and no wear on the counter surfaces was noted. Some researchers studied a mixture of nano-additive calcium borate with ZDDP [28] and LaF_3 nanoparticle surface coated by organic compounds containing S and P [29]. They observed that the composites showed better tribological performance. A recent study mixed the ZDDP with CuO nanoparticles under concentrations a successfully improved the anti-wear properties [8]. However, the literature did not compare theses additives, conventional and nanoparticles, in terms of tribological response.

Although nanoparticles have been widely investigated as an alternative to replacing conventional EP additives, it is deemed essential to look at their tribological performance is similar or superior the other EP additives. Thus, this paper's purpose was to evaluate and compare conventional EP additives (ZDDP and sulfur) and nanoparticles (CuO and ZnO), as well as their compatibility with two base oils, in order to verify their tribological performance. It is hoped that this paper will provide useful insights into additive selection and lubricant formulation regarding environmental and tribological aspects.

2. Methodology

2.1. Preparation Lubricants

The nanoparticles used as additives in this study (ZnO and CuO) were synthesized and characterized according to Alves et al. [3]. The size and shape of nanoparticles were characterized by transmission electron microscope (TEM- JEOL-JEM 2100- JEOL Instruments, Peabody, MA, USA). The nanoparticles were dispersed in a small volume of ethanol and sonicated (SONICS model VCX 750 high power immersion sonicator with added energy of 400J / g) for 15 min. The size was measured according to Alves et al. [12].

The ZDDP and Active Sulfur, as well as base oils, were donated by Yorga Lubricants (São Paulo, Brazil). The information about these additives is described in Table 1 and about base oils in Table 2. Viscosity and density of oils were determined experimentally: the kinematic viscosity at 40 °C and 100 °C, while the viscosity index and density at 20 °C were measured, according to the ASTM D4072 standard, from the viscometer densimeter SM 3000.

Table 1. Description of EP additives studied.

Additives
Zinc dialkyl dithiophosphate (ZDDP)—it has in its composition 3.5% of sulfur, 1.9% of phosphorus, and 2.1% of zinc.
EP sulfur-phosphorus additive (chemical states—sulfide (S^{-2})) —sulfur active in high temperature

Table 2. Physical and chemical properties of synthetic and mineral lubricating oils.

Oil/ Parameters	Density (g/cm^3)	Viscosity (40–100 °C)	Flash Point (°C)	Viscosity Index
Mineral (Parafinic)	0.8474	52.55/7.64	176	108
Synthetic (PAO 40)	0.8303	51.84/8.87	170	150

The nanoparticles concentration used for both oils was 0.5%. This concentration was chosen based on good results obtained by some researchers [14,16,17,30,31]. The dispersion was carried out under magnetic stirring (90 rpm) for 4 h in an ultrasonic bath. According to Gulzar et al. [32], this dispersion method was widely used; these authors mentioned about 30 researches that have good results with this way of dispersion. Also, before each test, the lubricants were homogenized with high-speed mechanical stirring (rotation 1250 rpm, 8 min) and ultrasonic bath (power 100 W, 35 °C for 8 min). This procedure kept the suspensions of CuO and ZnO in lubricating oil uniform, even without the use of dispersant. The EP additives were added to each oil base in the concentration of 3.0% (in volume) under magnetic stirring (90 rpm) for 1 h, and this concentration was chosen based on results from [33–35].

2.2. Tribological Assessment

The tribological performance of all additives was investigated by High Frequency Reciprocating Test Rig (HFRR), as detailed in Figure 1. The test was performed at the ball sliding on disk contact under boundary lubrication. The description of the tribological pair (ball and disk) is described in Table 3. The discs were polished to minimize the roughness effects on nanoparticles act.

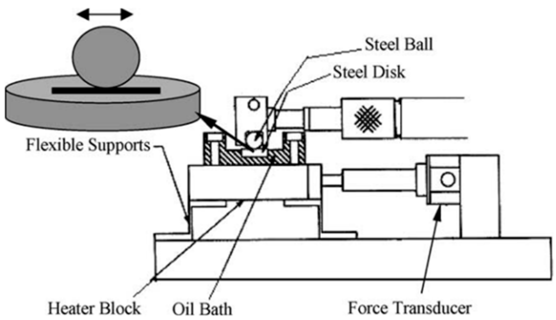


Figure 1. Schematic diagram of HFRR.

Table 3. Physical characteristics of tribological pair.

Parameters	Ball (AISI 52100 Stell)	Disk (AISI 52100 Stell)
Hardness (HV)	(570–750)	(190–210)
Dimensions	Diameter = 6.0 mm	Diameter = 10.0 mm Thickness = 3.0 mm
Roughness – Sa (μm)	0.04	0.02

The hard steel ball slides against the soft steel disk with 1.00 mm stroke length, at a frequency of 20 Hz, and a sliding velocity of 0.01 m/s for 60 min. The ball and disk in contact are fully submerged into 2.0 mL of lubricant at normal load of 10 N. The tests were performed in triplicate.

The lubricant temperature was kept at 50 °C in order to minimize the viscous effects of lubricant and to enhance the action of the nanoparticles. Also, various researches about EP additives are carried out in this range of temperature [12,14,20,21,23,25]. The friction coefficient was measured by a piezoelectric force transducer. The samples (balls and disks) had been cleaned with ethyl alcohol and acetone, as well as dried before and after the tests.

The tribological properties of synthetic (SO) and mineral (MO) oils were analyzed in terms of coefficient of friction (COF), wear scar diameter (WSD) of the ball, and the worn track in the disk. The investigation of the morphology and chemical element distribution of the worn surfaces was carried out in scanning electron microscopy (SEM) from Hitachi TM3000 (Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS). For this, it was employed an acceleration voltage of 20 kV. Also, the images of the worn surface were obtained in secondary electron (SE) mode.

3. Results and Discussion

3.1. Chemical Composition, Shape, and Size of Nanoparticles

The TEM image and X-Ray spectra of nanoparticles are presented in Figure 4. The size of the CuO and ZnO nanoparticles was around 4.5 nm and 10 nm, respectively, and their shape is near-spherical, as can be seen in TEM images (Figure 2)

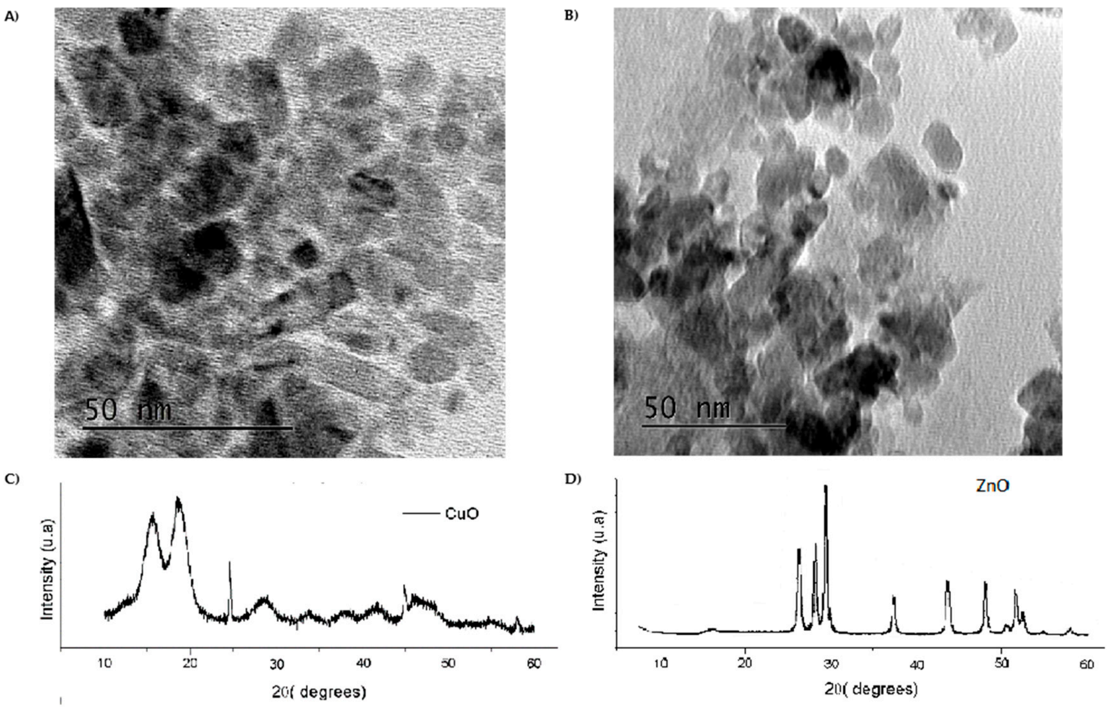


Figure 2. Size, shape, and chemical composition of nanoparticles: (**A**) TEM image of CuO; (**B**) TEM image of ZnO; (**C**) X-ray spectra of CuO and (**D**) X-ray spectra of ZnO.

In terms of chemical composition, the diffraction pattern of the samples with CuO (Figure 2c) and ZnO (Figure 2d) showed pure phases and all diffraction peaks indexed to the hexagonal structure with space group P63mc (ZnO) and monoclinic structure with group space Cc (CuO). These data are following the graph JCPDS # 75-0576 for the zinc oxide, and #80-1916 for copper oxide.

3.2. Tribological Assessment of HFRR

From Figure 3, it is possible to note that the nanoparticles exhibited different responses with respect to the anti-wear and low friction function, and it is dependent on their affinity with the oil base. ZDDP, for example, was more useful to reduce wear in both oils, but it is no effective to reduce friction. ZDDP is known for its anti-wear properties, but high friction coefficients are obtained at high temperatures [36]. According to [6,37,38], conventional EP additives containing zinc react at high temperatures with the metal surface preventing the welding of high points of the surfaces, or adsorption can occur on the metal surface protecting it from deeper wear.

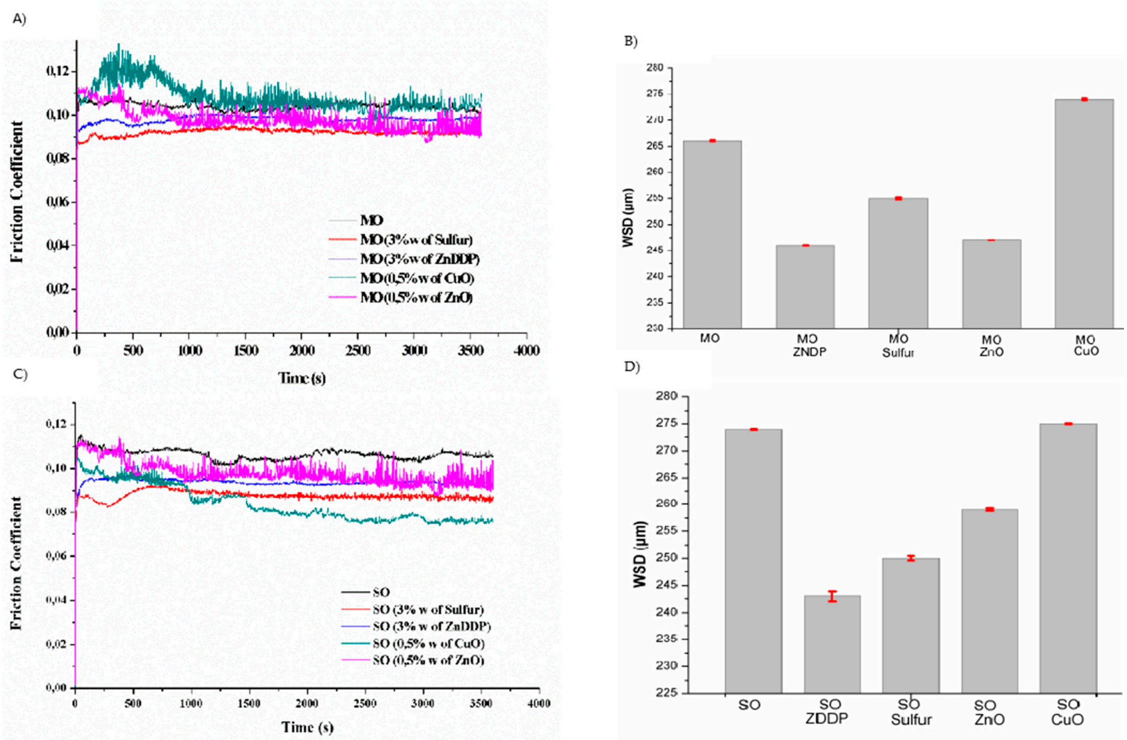


Figure 3. Tribological properties of lubricants without and with additives: (**A**) Friction coefficient behavior of base mineral oil lubricants, (**B**) Friction coefficient behavior of base synthetic oil lubricants, (**C**) WSD of base mineral oil lubricants and (**D**) WSD of base mineral oil lubricants.

The sulfur additive shows the low friction properties for both oils. Sulfur obtained a coefficient of friction value around 0.09 for both oils (mineral and synthetic), it can be concluded that it is an important active element in the boundary lubrication regardless of the lubricant bases. This occurred due to the conventional extreme pressure additive (Sulfur-) reacting with the metal surface when the lubricant film is ruptured and, thus, prevents higher friction and decrease wear. When the pressure applied to the oil film exceeds certain limits, and when the high pressure is composed of an extreme sliding action, the oil film breaks down, and there is a metal to metal contact. If the lubricant has an extreme pressure additive, with the disruption of the film, this additive reacts with metal surfaces forming a lubricating film [11,37]. The sulfur in the EP additive immediately reacts with the free atoms of surfaces forming a sulfide layer on them. This compound covering the metal surfaces protects them from the accession phenomenon [6]. In synthetic oil, as previously stated, the behavior exhibited by the ZDDP and Sulfur is similar to mineral oil, as verified by [39], even in low concentrations.

The interesting fact is that the nanoparticles used exhibited different properties according to the base oil. The ZnO nanoparticles show more affinity to mineral oil, presenting the anti-wear results that can be compared to the ZnDDP additives (Figure 3b) and low friction property similar to the sulfur (Figure 3a). On the other hand, synthetic oil did not show the same good results. However, it presented a small decrease in friction and wear.

According to [3], the anti-wear ZnO nanoparticles mechanism associated with the oil used, being better for the mineral base oil, also suggested that the deposition of nanoparticles on the surface might have formed a physical tribological film. A combination of four effects explains the excellent friction and wear properties of nanoparticles in the base oil, such as small nanoparticles, which interact with the friction surfaces and form a protection film, spherical geometry that is most likely to change the sliding friction to rolling, and low concentration of nanoparticles that can interfere with the increasing or decreasing friction and deposition on the surface [40]. This result is promised because ZnO additives have not the phosphates and sulfur in this composition that makes it less toxic and environmentally friendly. Both properties are observed when ZnO was used in mineral oil, presenting similar results to sulfur. It is important to note that the sulfur does not display effective anti-wear properties.

While for the mineral oil, the CuO did not show the same behavior as ZnO, with a higher friction coefficient being observed, i.e., around 0.11, and WSD did not display effective anti-wear or low friction properties. The third body mechanism can explain a possible reason for the behaviour of nanoparticles [41]. This fact is associated sometime to the poor dispersions of nanoparticles in oil or incompatibility with oil [17] described by a weak molecular interaction of the nanoparticle with the base fluid resulting in the re-agglomeration of nanoparticles [20]. Nevertheless, the nanolubrication mechanisms may suffer the influence of the nanoparticles size and concentration, and they have different effects on the tribological performance according to the nanoparticle nature [14]. On the other hand, the copper oxide nanoparticles gave low friction properties for synthetic base oil with the first decrease the coefficient of friction around 1000 s similar to sulfur (in Figure 3c). This additive presents a new friction reduction after 1500 s with a 30% reduction. Probably, such a change was due to another nanolubrication mechanism, in that the nanoparticles are deposited on the surfaces in contact, compensating the mass loss by the "mending effect" [18]. This mechanism was reported to CuO nanoparticles as an additive to PAO [14,20]. It may be associated with their interaction with this oil, as discussed above. The compensating the mass loss is supported by the presence of the CuO in the worn surface, shown in the EDS analysis (Figure 4f). This fact makes this additive similar to sulfur, which had good results in both oils studied in this work. According to [1], the oxide nanoparticles penetrate the contact zone and are deposited on the surface because they are smaller or similar in size with lubricant film, improving the lubricating performance. The elliptical shape of the wear scar printed on the ball by all samples suggests material accumulated on the side of the worn track [42].

In summary, Copper oxides have more affinity with the synthetic oil, as observed by [3,20,21,23], while zinc oxides have an affinity for mineral oils. However, oxide nanoparticles can entirely replace the extreme pressure additives, obtaining similar results, improving the tribological performance (low friction and anti-wear) and meeting the new environmental standards, reducing its damage. The average friction coefficient and WSD are summarized in Table 4 to verify its repeatability.

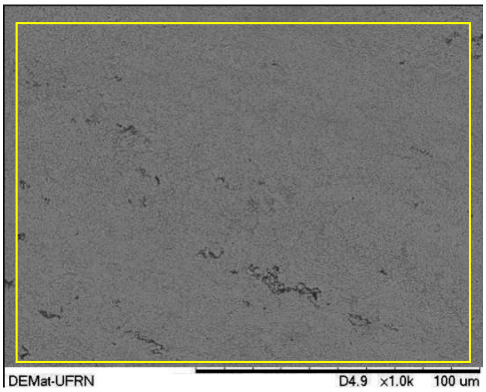
Table 4. Tribological performance properties exhibited by the investigated lubricants.

Oils with Additives		Average Friction Coefficient		WSD (µm)	
SO pure	MO pure	0.106 ± 0.003	0.104 ± 0.003	274	266
SO + ZDDP	MO + ZDDP	0.094 ± 0.002	0.097 ± 0.003	243	246
SO + Sulfur	MO + Sulfur	0.087 ± 0.003	0.092 ± 0.002	250	255
SO + ZnO	MO + ZnO	0.097 ± 0.005	0.099 ± 0.006	259	247
SO + CuO	MO + CuO	0.080 ± 0.008	0.108 ± 0.007	275	274

* The Average Friction coefficient was calculated by a simple average of three repetitions, each one with 3600 points acquired every second.

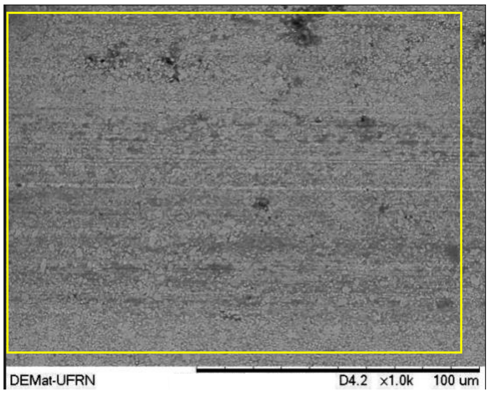
3.3. *Morphological and Chemical Surfaces Analyses*

The characteristics of the surfaces after the tribological test were evaluated by SEM images in Figure 4a–j and EDS spectrum in order to understand the action mechanism of EP additives.



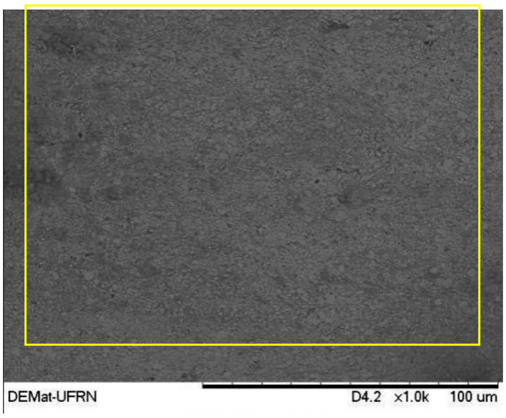
Element	Weight %
Chromium	4.6
Iron	94.4
Others	0.9

(A) Synthetic Oil



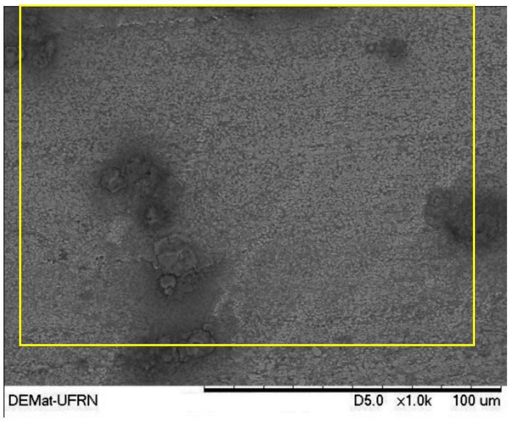
Element	Weight %
Chromium	1.7
Iron	54.5
Oxygen	42.8
Others	1.1

(B) Mineral Oil



Element	Weight %
Iron	52.5
Sulfur	1.2
Oxygen	4.6

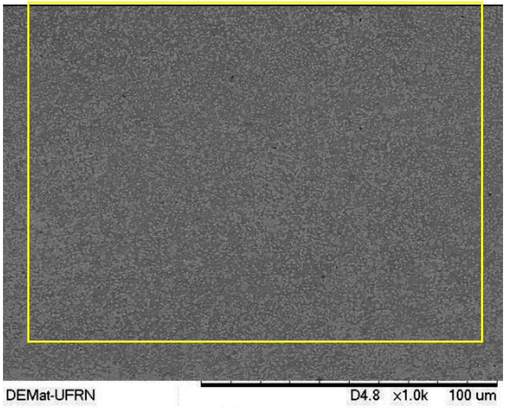
(C) Synthetic Oil (ZDDP)



Element	Weight %
Iron	67.9
Zinc	1.7
Sulfur	2.3
Oxygen	26.0
Others	1.9

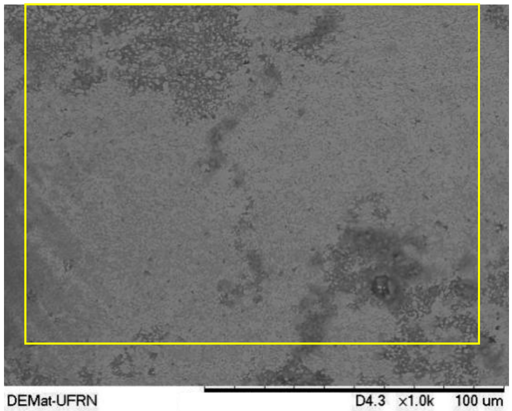
(D) Mineral Oil (ZDDP)

Figure 4. *Cont.*



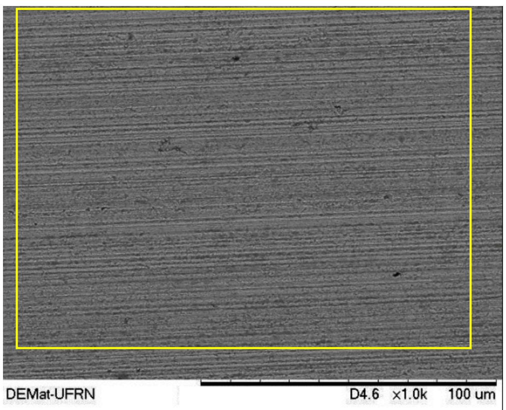
Element	Weight %
Iron	78.5
Sulfur	9.1
Oxygen	9.6
Others	2.8

(E) Synthetic Oil (Sulfur)



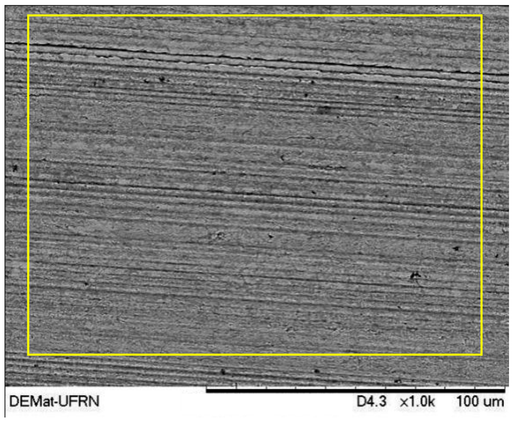
Element	Weight %
Iron	57.5
Sulfur	3.1
Oxygen	36.7
Others	2.6

(F) Mineral Oil (Sulfur)



Element	Weight %
Iron	74.5
Oxygen	22.7
Copper	1.8
Others	1.0

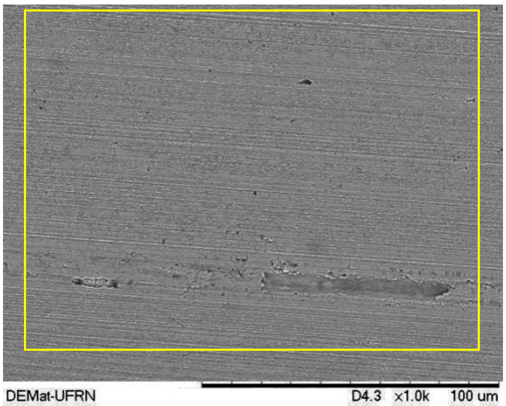
(G) Synthetic Oil (CuO)



Element	Weight %
Iron	72.4
Oxygen	4.5
Others	1.1

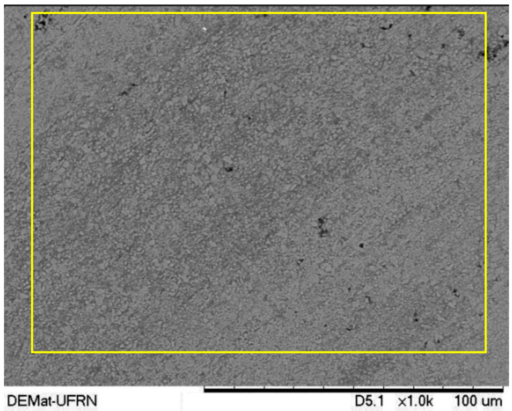
(H) Mineral Oil (CuO)

Figure 4. *Cont.*



Element	Weight %
Iron	71.3
Oxygen	27.1
Others	1.6

(I) Synthetic Oil (ZnO)



Element	Weight %
Iron	76.1
Oxygen	20.2
Zinc	0.8
Others	2.9

(J) Mineral Oil (ZnO)

Figure 4. SEM images and EDS analysis of the worn surfaces for: (**A**) Synthetic oil, (**B**) Mineral Oil, (**C**) Synthetic oil + ZDDP, (**D**) Mineral oil + ZDDP, (**E**) Synthetic oil + Sulfur, (**F**) Mineral oil + Sulfur, (**G**) Synthetic oil + CuO, (**H**) Mineral oil + CuO, (**I**) Synthetic oil + ZnO and (**J**) Mineral oil + ZnO.

Figure 4a,c,e,g,i displays SEM images of wear surface lubricated with synthetic oil. As can be seen in Figure 4g,h, the wear mechanism is strongly influenced by the type of EP additives. More scratches in sliding directions are identified when CuO nanooxides acts as EP additives, this morphology evidences abrasive wear mechanism. However, there is a clear reduction of damage when using the CuO with synthetic oil (Figure 4g) in comparison to the mineral oil (Figure 4h), where it is possible to observe deep wear on the surface. SEM is an analysis of the worn morphology to evaluate the anti-wear properties. The copper oxide behavior in synthetic oil modified the wear morphology and presented higher WSD value than all other additives and the pure synthetic oil, but the smallest coefficient of friction measured in this study was observed for the addition of copper oxide nanoparticles in synthetic oil. This behavior can be associated with the concentration used in this work. High wear was seen for worn nanolubricant with 0.5 wt% of CuO by [7] and [14]. The EDS analysis showed the presence of cooper that promotes a protective film of CuO, decreasing the friction by the mass loss compensation mechanism known as the "mending effect", proven by the presence of copper (EDS analysis) on the worn surface. Thus, based on this statement, it can be concluded that CuO nanoparticles act as a friction reducer to the synthetic oil, but do not exhibit anti-wear ability.

On the other hand, the CuO in mineral oil behaved as a third body associated with the hardness of the nanoparticles (Figure 4h) [1]. The morphology of the surface shows more damage, suggesting that debris have been extruded out from the worn surface. The third body effect characterizes the change in morphology and justifies the marks of abrasive action in the mineral oil. The analysis of the EDS made on the surface of Figure 4h demonstrated that there was no presence of copper nanoparticles, and they have not been deposited on the surface because the surface exhibits low roughness. Thus, it may be worked as a third body in the metal, causing the scratching, and after they were withdrawn from the contact, it presented the worst result for friction and wear, confirming the higher coefficient of friction value from the graph (Figure 4a). For this oil, the CuO nanoparticles should not be used in this concentration and dispersion condition.

In the case of the ZnO added in the synthetic oil, the morphology (Figure 4i) shows a plastic deformation and adhesive wear mechanism like was just observed a reduction in WDS on this sample. However, the coefficient of friction had not any significant reduction concerning pure oil. It suggests that this additive behaves as an anti-wear additive, but not as friction reducer when combined with synthetic oil. Considering only the SEM images from oils with ZnO nanoparticles, Figure 4j showed fewer wear marks compared to other EP additives. As aforementioned, the zinc content value found on the worn surface indicates that zinc oxide nanoparticles combined with mineral oil formed a tribofilm and protected the surface against severe wear.

The presence of the components from the ZDDP additive in the EDS analysis (Figure 4d) confirms that this additive reacted with the surface, reducing the wear on the disc and ball (demonstrated in WSD results). Also, some oxidation signals were confirmed by the high oxygen concentration in the EDS analysis. The same behavior was observed in the case of Sulfur additive (Figure 4e,f), however with a low oxygen concentration on surface, minimizing the oxidative wear. Thus, the wear surface is smooth and with few grooves. This observation accords with the values of the WSD, while the friction coefficient confirms that sulfur demonstrated anti-wear and low friction ability.

The wear mechanism depends on the base oil, as can be seen in Figure 4b,d,f,h,j whereby mineral oil was used. It was possible to verify signals of the oxidative, abrasive, and adhesive wear mechanisms. The conventional EP addition on mineral oil promoted more oxidative wear than synthetic oil base. This statement is supported by EDS analysis, while the percentage of oxygen in the wear track is 36% higher than Sulfur additives and 26% higher than ZDDP. Besides the oxidation, the lubrication film was formed, generating a smoother surface with a few superficial scars. This fact is verified by the presence of sulfur and zinc in EDS. These observations corroborate with the friction coefficient and WSD. Both additives act as anti-wear and friction was reduced when compared to pure mineral oil.

From the aforementioned results, the film formation ability of nanoparticles studied depends on the synergism with base oils. When there is this synergism, the worn surface was relatively smooth, with only slight signs of wear for the combination CuO in synthetic oil and ZnO in mineral oil. Moreover, the CuO nanoparticles are the most suitable synthetic oil, resulting in less friction. On the other hand, mineral oil had the best performance when ZnO was added. In this case, smaller wear was observed, like the ZDDP. Moreover, the wear analysis considering oil and nanoparticles corroborates with results of friction coefficient discussed above.

4. Conclusions

Based on the results and discussions previously addressed, it is possible to conclude:

- The additives EP (ZDDP) in the contact between surfaces (metal-metal) presented good performance as anti-wear in both lubricant bases.
- The sulfur additive served to decrease friction, as a low friction additive, but did not have useful anti-wear characteristics.
- For the zinc oxides nanoparticles, the formation of a protective film can be observed by adhesion on the surface. The SEM images showed a homogeneous surface comparable between the other additives. Its performance was similar to ZDDP, as the protective film was formed and served as a good anti-wear and low friction additive, more effective for a mineral lubricant base.
- The CuO nanoparticles in the synthetic lubricant base obtained better results in reducing the coefficient of friction between all other results and suggest that it is a great low friction additive.
- The oxide nanoparticles function differently in base oils. Depending on the oil, these additives improve or worsen the lubricant performance.

Generally, the results showed that, in terms of tribological performance, nanoparticles were no more effective than conventional EP additives. However, they achieved similar results. Regarding the environmental aspects, the nanooxides (ZnO and CuO) were more suitable than traditional additives.

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