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Study on the anti-wear properties of metal-forming lubricants with TiO2 and CuO nanoparticle additives

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Abstract. The metal-mechanic industry is intensive in operations of transformation of materials that demand a high energy consumption to overcome the coefficient of friction (COF) generated in the manufacturing process. One of the most demanding processes is the deep drawing forming process of chassis for the automotive industry. Every day more resistant and lighter steels are developed with the aim of contributing to the efficiency in the use of fuel. The problem is generated by having a speed of development of structural steels greater than that of tool steels; these (tool steels) suffer the consequences: wear and fractures as well as increases in the COF. Currently, the aim is to reduce the coefficient of friction and the wear generated by several technologies: a) surface engineering with coatings, surface thermal treatments and laser texturing among others. b) In addition, work is being done to produce lubricants that are more efficient and to reduce the COF and wear to the maximum. It is well known that lubrication is essential for protecting moving surfaces against friction and wear in metalworking applications. Nanotechnology is a science that is improving the tribological performance of lubricants in big leaps through the addition of nanoparticles in concentrations ranging from 0.01 wt.% to 2 wt. %. In this work one metal-working polymeric lubricant with viscosity of 529 Cst, was treated with varying wt.% (0.01, 0.05 and 0.1) of CuO and TiO2 nanoparticle additives. Anti-wear properties of wear scar diameter (WSD) and coefficient of friction (COF) were characterized with a four-ball T-02 tribotester according to ASTM D 5183 and with a ball-on-disk apparatus. The dispersion method used for combining nanoparticles and lubricant also is explained. Nanoparticle additives showed an overall improvement of the tribological properties of polymeric lubricant. An important improvement of anti-wear properties for CuO at 0.05 wt.% and TiO2 at 0.01 wt.% of 33% and 77%, respectively, (WSD improvement) were obtained demonstrating the potential of nanolubricants for improving the efficiency of mechanical components. This work in addition to showing the improvements found presents the possible tribological mechanisms that explain the anti-wear behavior obtained in the laboratory.

1. Introduction

For decades inorganic additives in lubricants at microscale applications for anti-wear (AW) have been used, however the number of applications with the same additives but the use nano-metric additives scale has grown considerably in recent years [1, 2] because to the substantial improvements that are present in low coefficient of friction (COF) and anti-wear (AW) properties applications. In the literature review a lot of information about the causes of the benefits in tribo-metrics properties of nanofluids by incorporating inorganic nanoparticles as CuO and TiO2 can be found; some of them are mending effect, creation of tribo-films, decreasing contact pressures in order to have larger surface contact areas among the others [3].

Table 1 shows some research published in recent years in which additives of inorganic nanoparticles in nanoscale shown reductions in the coefficient of friction (COF) and reductions in wear scare diameter of the samples studied (WSD).

Table 1.WSD and COF decrease using additives (inorganic nano-particles) in lubricant.

Nano-particle	Concen-tration (wt.%)	Fluid	Improvement in WSD	Reduction of COF	Reference
CuO	2%	PAO6	60%	50%	Hernández et al. 2010 [4]
CuO	1%	Epoxy resin	-	35%	Larsen et al. 2007 [5]
ZrO_2	0.5%	PAO6	27%	-	Hernández et al. 2008 [6]
TiO_2	1%	Base Oil	-	15%	Hu et al. 1997[7]
TiO_2	0.1%	Oil	11.78%	13.23%	Luo et al. 2014[8]
Mg3(BO3)2	1%	Base Oil	30%		Hu et al. 2002 [9]
Ti	250 ppm	SJ15W40	50%	-	M. Vijayaraj et al. 2016 [10]

Many other authors similarly show the benefits of using CuO and TiO2 as inorganic nano - additives in lubricants since diminish the pollution created by sulfides currently used as additives in many mechanical and engine motors applications [10, 11, 12].

The behavior of the CuO and titanium TiO2 nanoparticles regarding their concentration and dispersion within a polymeric lubricant is studied in the present work in order to reduce COF and wear for metal-forming operations.

2. Materials and test methods

2.1. Materials

Nano-lubricants were prepared with three different concentrations (0.01, 0.05 and 0.10 wt%) of CuO and TiO2 nanoparticles within a based lubricant (polymeric lubricant). The utilized nanoparticles are obtained (table 2) as a dry powder through chemical or physical methods. CuO & and TiO2 nanoparticles (Sigma Aldrich) are then introduced into the designated fluid and dispersed using an extended bath sonication (5 minutes) in order to achieve a full dispersion of the particles within the fluid. Samples may be subject before testing to a Cole-Parmer 500-W ultrasonic probe sonicator for 2.5 minutes in order to avoid any residual agglomerations. Such concentrations rates were chosen due to previous research [13], were a significant improvement in the tribological properties have been noticeable within low concentration ranges of nanoparticles.

Table 2. Material properties.

Materials	Properties		
Base Fluid	**Density**	**Viscosity**	**Application**
polymeric lubricant	1.090 g/cm³	520.14 Cst	Metal Stamping lubricant
Nanoparticles	**Morphology**	**Size (nm)**	**Hardness**
Copper Oxide (CuO)	Spherical	<50 nm	3.5 Mohs
Titanium Dioxide (TiO_2)	Spherical <21		6.0 Mohs

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2.2 Test Methods

The tribotesters used to determine the performance properties of the lubricant were the tribotester with a four-ball fixture (T-02) and the ball on disc (T-11) as shown in figure 1. The basic procedure for the T-02 tribotester consists of a ball which rotates while applying pressure with a load P and a rotating speed n on three fixed balls secured by a holder as shown in figure 1. Used test balls were an AISI 52100 chromium alloy bearing steel with a diameter of 12.7 mm (0.5 in.) and a hardness of 60-65 HRC.

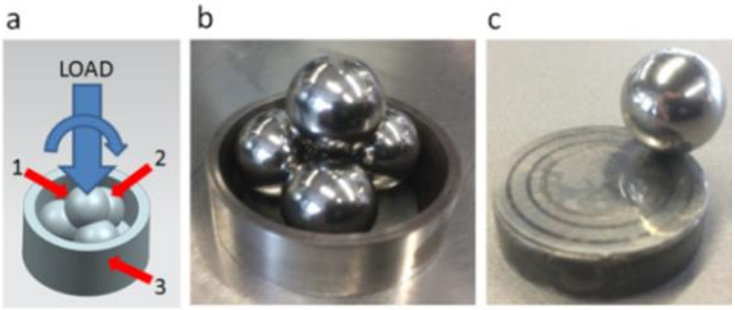

Figure 1. (a) and (b) Operation System of the T-02 Tribotester: (1) upper and rotating ball loaded, (2) lower balls, (3) oil container, (c) T-11 pin of ball on disk geometric friction pair, [14,15].

For the T-02 tribotester, the ASTM D 5183 [16] was conducted. This method consist of a constant load of 392 N is applied to the fixed bearings for a lapse of 60 minutes, while an electrical resistance heats the holder and maintains it at a constant 75°C temperature. This test is used to determine the anti-wear properties of a lubricant.

The other tribotester used based on ASTM G -99, T-11, utilized a different fixture [17]. A ball bearing with a diameter of 0.25 in is placed over a rotating D2 quenched steel disc. A constant load of 25 N is placed over the bearing, aiding in the study of the anti-wear properties of a lubricant. A change in the distance radius must be made in order to reuse the disc up to three times. Because this tribometer (T-11) is not prepared to keep lubricant into the chamber we proceeded to feed the surface with 2ml of lubricant every 1,000 seconds in order to maintain constant levels of COF throughout the test. The test was monitored at all time and the values of COF and wear of the tribosystem was maintained stable as shown in figure 2. Table 3 displays the tests parameters used in this research for both tribotesters.

Table 3.Tribotesters tests parameters.

Parameters	ASTM D5183 (T-02)	Ball on disk (T-11)
Time	60 min	3,000 s
Velocity (RPM)	600	318, 455, 800
Temperature (ºC)	75	23
Applied force (N)	392	25
Wear track distance (m)	-	1000 m
Wear track radius (mm)	-	10, 7, 4
Time interval to add lubricant (s)	-	1,000

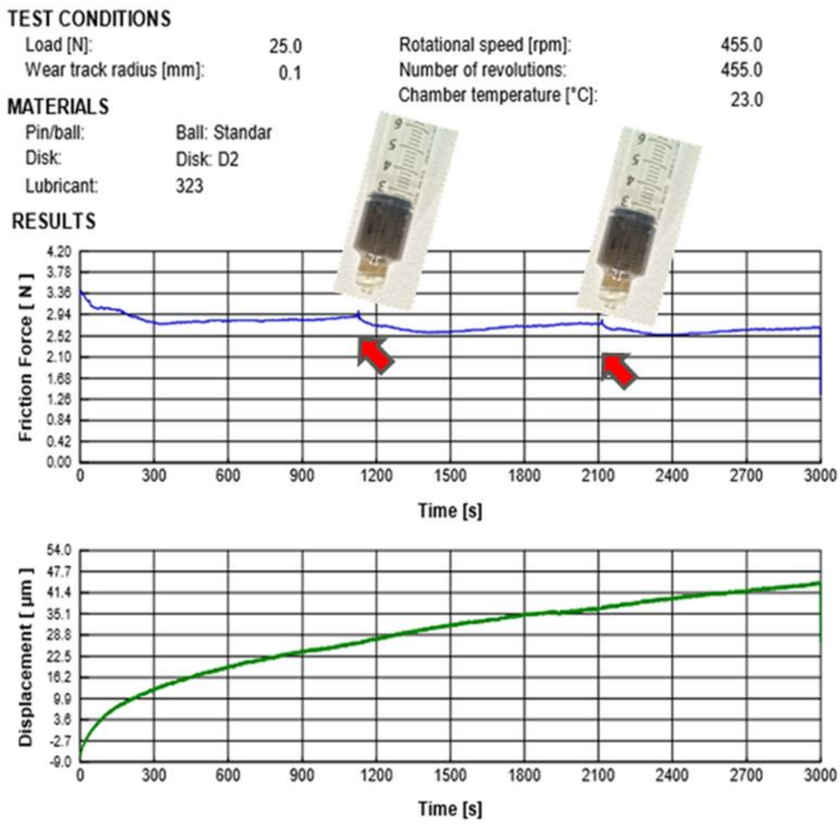

Figure 2. Graph showing the behavior of COF during the time of the test.

3. Results and Discussion

For the ASTM 5183 test only in some cases small reductions were obtained in ranges from 4% to 6 % in WSD at concentrations of 0.05 wt. % in both materials. The results graph is shown in figure 3.

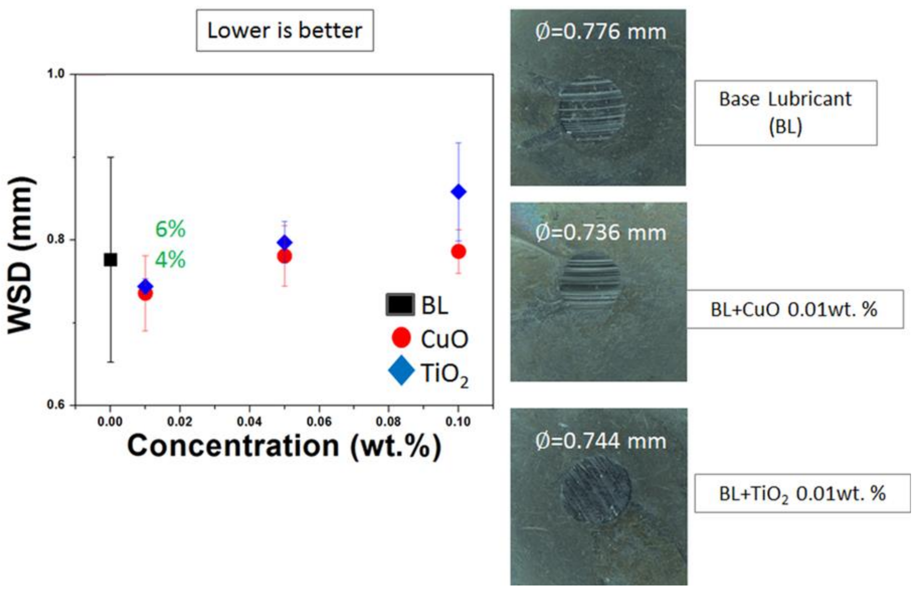

Figure 3. Test results for ASTM 5183 with associated WSD for each wt% concentration.

In this test a tendency to increase the WSD is observed with increasing wt. % of both materials probably because of agglomeration of nanoparticles in base lubricant. Finally the results of wear tests on the pin on disk shown a significant improvement in reducing wear on the disk to such a degree that it was almost imperceptible, in this situation the G99 [17] standard allows measurement of WSD on the ball. Figure 4 shows a comparison of the wear track generated in dry conditions and then generated in lubricated conditions because of the improved of nanoadditives.

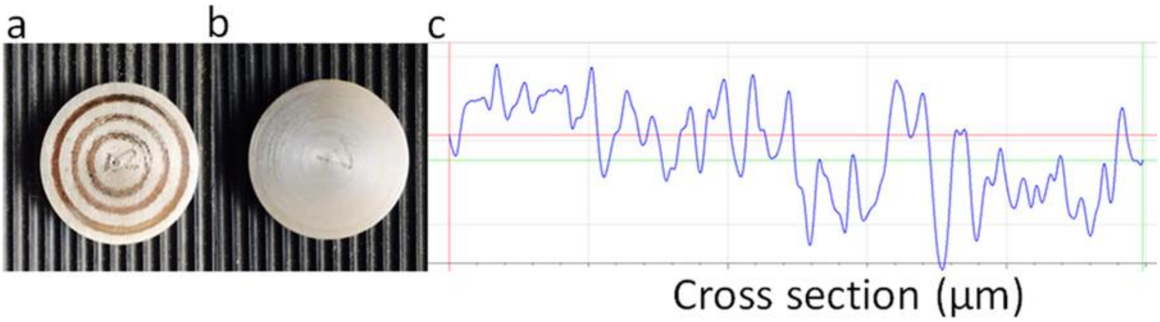

Figure 4. (a) Wear track in dry conditions, (b) Wear track of disk with lubricant and 0.05 wt. % of CuO, (b) Cross section of the wear track with a surface analyzer.

The graphs of the COF results versus time can be seen in figure 5. In the case of CuO decrease COF for 0.05 wt. %, but not significantly; in the case of TiO_2 it can be noticed that at 0.01 wt. % COF is reduced in a considerable amount. This is associated with the decrease of the ball WSD.

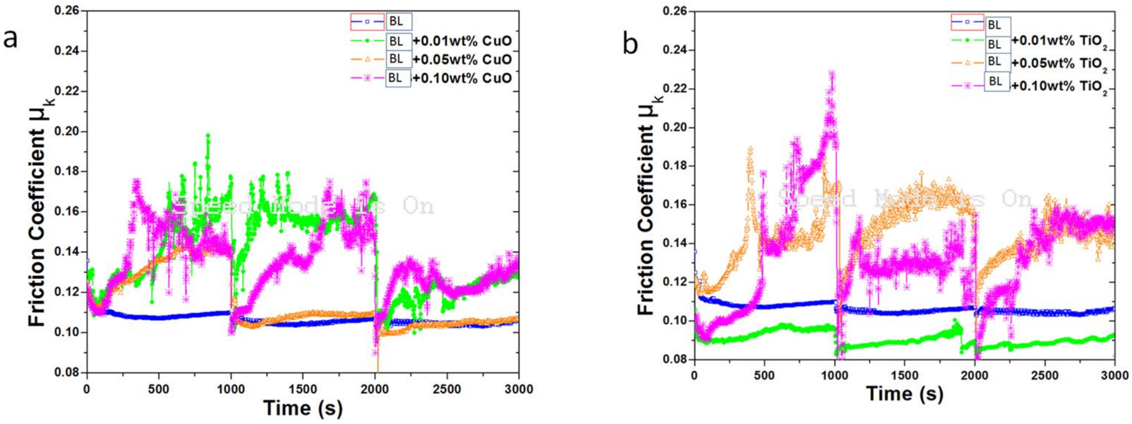

Figure 5. COF graphs for (a) CuO and (b) TiO_2.

Figure 6 shows that the worn area decreases in both materials, in the case of CuO the largest decrease was observed in the 0.05 wt. % with a 33% of decrease compared with the base oil, in the case of TiO2 nanoparticles have decreased to 77% for the 0.01 wt. %. Overall there is a trend to increased wear with increasing of wt. %.

The results show an improvement in the wear on the CuO particles when presenting a less WSD (Figure 3) when load of 392 N was applied; since being a softer material tends to create an exfoliating layer or a possible tribo-sinterization that would need to be characterized between the surfaces according to what was reported by Hernandéz Bates [4], on the other hand at lower loads (25 N) the TiO2 particles that due to their hardness, show better wear results by functioning as a third body that could function as valley filler, bearing effect or spacer [7].

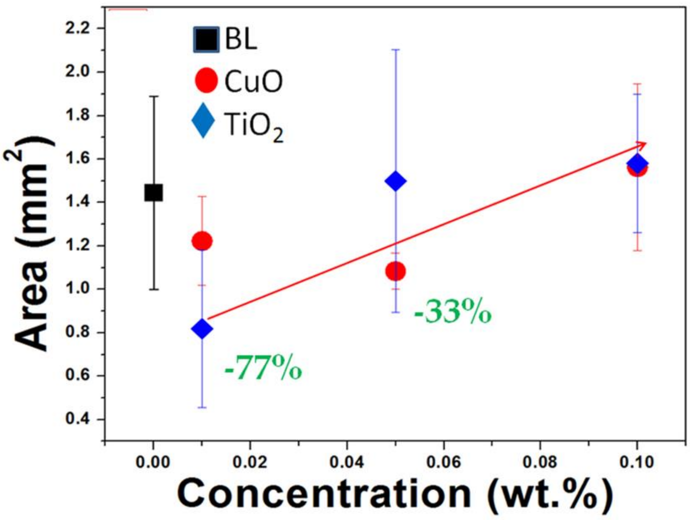

Figure 6. Worn area graph over the ball for both materials (mm2 on wear ball).

4. Conclusions

Tribological properties for the polymeric lubricant were determined with 0.01, 0.05 and 0.10 wt % of CuO and TiO2 nanoparticles. In the case of ASTM 5183 test, only small increments up to 6% in the case of CuO at 0.01 wt% was found, likely due to the agglomeration of nanoparticles due to the high temperatures or because tribo-sinterization and the filling of cavities by the nanoparticles was oversaturated. For G 99 test (ball on disk), high improvements on WSD on the ball were founded, 33% for CuO at 0.05 wt. % and up to 77% for TiO2 at 0.01 wt. %. In this case the filling of cavities by the nanoparticles was over saturate and the nanoparticles act as abrasive wear agent for the ball. It is recommended to investigate use of dispersants to minimize agglomeration and precipitation. This shows the potential of nanofluids and the opportunity for further investigations with other nanoparticles.

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