23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

EFFECT OF DISPERSANT AGENT IN ANTIWEAR ABILITY OF OXIDES NANOPARTICLES IN LUBRICANTS

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Abstract. *Oxide nanoparticles (NNP) have been used as extreme pressure additives in boundary lubrication, with good results. However, the major challenge of this technology is to control the NNP dispersion in base oil. An uncontrolled agglomeration of these nanoparticles may cancel its antiwear ability, besides they can increase the friction between metallic surfaces. This article aims to study the effect of organic dispersants to enable a better performance from NNP as an antiwear additive in lubricants. Copper oxides at the nanoscale were dispersed in lubricant base with using three organic solvents as dispersive agents (Toluene, Hexane and Ethylene Glycol). The dispersion was evaluated by UV visible spectroscopy tests and visual analysis. The dispersed samples were submitted to a test with relative contact between two metal surfaces to verify the effect on the antiwear action. The tribological tests were carried out in HFRR tribometer. The UV visible results showed more uniform size distribution of the NNP dispersed in lubricant oil when toluene was dispersant agent. Furthermore, this dispersant provided a substantial decrease of the coefficient of friction, as well lower abrasion losses in the tribological tests.*

Keywords: *Nanoparticles, dispersant, friction reduction.*

1. INTRODUCTION

Improving the physical and chemical properties of materials is the goal of many researches. Currently, nanoparticles have aroused interest in this field, since it has superior properties that can be manipulated to the desired applications. In Mechanics, the metal nanoparticles stand out as additives in lubricants, giving anti-wear properties and promoting the reduction the friction (Jadhav *et al.*, 2011; Zin *et al.*, 2013; Battez *et al.*, 2008).

Among several metallic nanoparticles the copper oxide nanoparticles have been paid attention for its mechanical properties (Sankar *et al.*, 2014). Its crystalline and chemical structures make these nanoparticles more actives on the protection film formation by rolling action on the surface (Zin *et al.*, 2013).

The success of the nanoparticles depends on a number of parameters such as particle size, shape, concentration and dispersion or yet the chemical interaction with the oil in the system (Wu and Kao, 2011; Xu, 2008). The smallest sizes of these metal nanoparticles are more susceptible to increase anti-wear efficiency and reduce friction (Wu and Kao, 2011).

A main challenge in using nanoparticles is related to their dispersion in liquids because the metal nanoparticles easily agglomerate due to their high surface tension. This agglomeration results in many problems, such as clogging and contact starvation (Rabaso *et al.*, 2014). According to Xu (2008) dispersing nanoparticles into individual particles it is not an easy task and can be a complicated process.

In order to minimize the metal nanoparticles agglomeration, Laurent *et al*. (2008) found a good dispersion of magnetite nanoparticles with toluene and hexane; Pãcurariu *et al*. (2014) found good dispersion of maghemite nanoparticles in toluene; Knecht *et al*. (2006) obtained encapsulated nickel nanoparticles with solubility in toluene; Wu and Kao (2011) dispersed TiO_2 nanoparticles in lubricants with Ethylene Glycol, reducing the aggregation after preparing the particles; Heath *et al*. (1996) obtained spherical gold encapsulated nanoparticles and stable for months in toluene.

This study aims to evaluate the effect of organic dispersants for achieving a better performance of the NNP as anti-wear additive in lubricants.

2. EXPERIMENTAL AND METHODS

2.1. Synthesis and characterization of copper oxide nanoparticles

Two solutions for the synthesis of nanoparticles were prepared: one ethanoic solution of copper acetate, in which were dissolved 2 mmol of copper acetate monohydrate in 40 mL of ethanol, and another ethanoic solution with sodium hydroxide, 8 mmol of NaOH dissolved in 40 ml of ethanol. In a teflon reactor, 10 ml of each solution were mixed and reacted in the microwave oven (Panasonic NN562BK) at 99 watts power for 140s, pulse on / off 20 to 10 sec. This pulse was repeated nine times to maintain the temperature of 80 ° C. The reactor was cooled to 15 ° C for 5 min, then the nanoparticles were recovered from the suspension by centrifugation for 5 min. After that, they were washed with warm water and returned to the centrifugation, repeating the washings and centrifugation. Finally, the recovered washing was performed with ethanol, centrifuged for 5 min and dried in an oven at 60 ° C for 2 h or until all ethanol was evaporated.

To improve dispersion of the nanoparticles, these were encapsulated with oleic acid. 0.2g of CuO nanoparticles were mixed with 0.01g of oleic acid and 20 ml of ethanol. It was stirred for 2 h at a temperature of 60°C and after centrifuged for 10 min. After this time, they were dried in an oven for 2 h or until all ethanol was evaporated.

Afterwards, the produced samples were characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM). The X-ray diffraction analyses were carried out using a XRD-6000 powder diffractometer with Cu Kα radiation, operating at 30 kV and 30 m, in the range from 201 to 701 with 0.021 / min. Subsequently, the crystallite size was calculated using the Scherrer's equation $D_{hkl}=k\lambda/\beta \cos\theta$, where D_{hkl} is the crystallite size, k is the sphere shape factor (0.89), θ is the angle of the diffraction, β is the full width at half-maximum (FWHM) of the peak and λ is the wavelength of X-ray (1.54056Å).

2.2. Additive

Used was 0.1% by weight of copper oxide nanoparticles in magnetic stirring for 6h at 20°C in the synthetic oil (PAO) with three fractions of dispersant: 2 ml of toluene to 8 ml of the oil; 0.2 ml to 8 ml Hexane oil and 0.8 ml Ethylene Glycol to 7.2 ml oil.

In the case of nanoparticles dispersed in Toluene and Hexane, after these were stirred solvent evaporated in an oven at 70°C for 24 h.

2.3. Analysis of the dispersion

The dispersion of nanoparticles was performed for each of the dispersants by visual analysis and characterization by UV-visible (after 30 days of preparation). This latter technique was used to verify the distribution of particles in the oil and still to check the spherical shape of NPN's, through the formation of plasmonic band characteristics. The analysis was done in the scan range 190-1100 nm UV-vis spectrophotometer Shimadzu (UV-1650pc). This procedure was performed before and after the tests in tribometer HFRR.

2.3.2. Experimental test of contact

Tribological performance tests were evaluated in tribometer HFRR (High Frequency Reciprocating Rig Test) operating with lubricated ball-plan reciprocating contact with ball 6.0 mm in diameter (570-750 HV) and a disc (190-210 HV 10mm Ra diameter and 0.0067 µm), both AISI 52100 steel. The test was conducted with the specimens submerged in 2 ml of the solutions tested under a constant temperature of 50 ° C in the course of 1.00 ± 0.02 (20 ± 1 Hz), and an applied normal load of 10 ± 0.01N. The tests were performed in triplicate, with a duration of 60 min each test. At the end of the experiment were analyzed and WSD coefficients of friction balls.

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction (XRD)

The sample X-ray diffraction analysis was shown in fig. 1. The crystallite size obtained was 5.3 nm, agreeing the results of Medeiros et al. (2014) that used the same reaction groups. Observed the presence of copper monoxide (monoclinic), obtaining samples of high crystallinity.

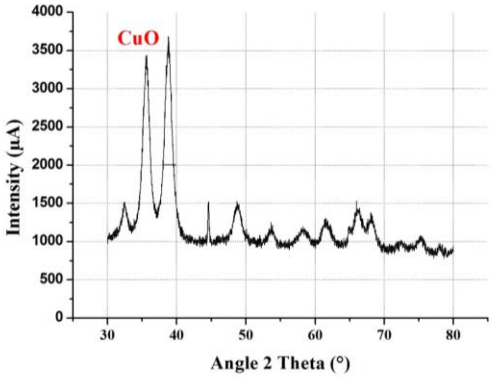

Figure 1. X-ray powder diffraction pattern of the prepared sample.

In the case pure phase was obtained and all diffraction peaks indexed to the mono-clinic structure with space group Cc (CuO). These data are in agreement with the JCPDS files #80-1916, copper oxide, begin the angles within the limits that characterize 35.7 to 38.5 ° according Rejith *and* Krishnan (2013), Whang *et al.* (2002), Liu *et al*. (2007) and Barbalho (2007).

3.2 Dispersion analysis of nanoparticles

3.2.1 Visual analysis of the dispersion of nanoparticles

Figure 2 shows the images with 0.1 wt% of copper oxide nanoparticles dispersed in three dispersants: Toluene, Hexane and Ethylene Glycol, respectively. The images were made after one month of dispersion.

Figure 2. Copper oxide nanoparticles dispersed in toluene, hexane and ethylene glycol, respectively.

The sample with toluene finds well dispersed, presenting a better result between the three, followed by ethylene glycol and finally hexane. The nanoparticles with toluene remained as colloid solutions (well dispersed) even after one month, without any notable change in their state of dispersion. A fact to be discussed for the samples dispersed in ethylene glycol is that sedimented nanoparticles return to their initial state (as toluene) after a brief manual agitation.

3.2.2 Analysis of dispersion of nanoparticles by Uv-visible spectrophotometer

The figure 3 shows the resonant spectra graph with plasmon band of copper oxide nanoparticles, dispersed in 0.1 wt% with three dispersing agents.

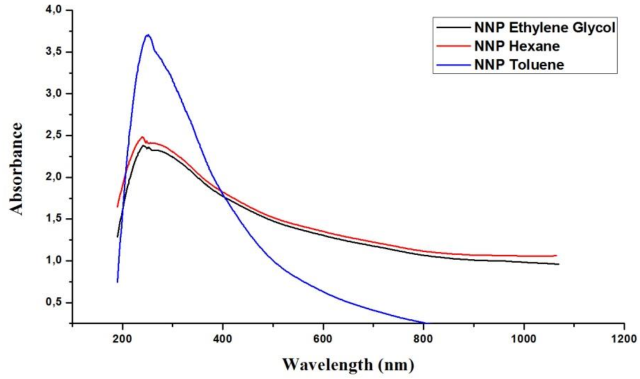

Figure 3. The UV–vis spectra.

The resonance plasmon spectrum (SPR) of all samples showed characteristic band of copper oxide in the spectral region between 240-300 nm, corroborating the results of Sankar *et al.* (2014), Logar et al (2014), Zhang and Yang (2013) and with the results XRD, indicating that the nanoparticulas are in fact cupric copper oxide (Dong *et al.*, 2014). The absence of the surface plasmon peak of copper at about 600 nm proves that all nanoparticles present are of copper oxide.

Other important result is related with metallic nanoparticles geometry, because the formation occurred just a plasmon band for all dispersants, suggesting that the nanoparticles has spherical geometry (Liz-Marzán *et al.*, 2004). Thus, it is not expected to be found any changes in its optical and electronic properties (Sankar *et al.*, 2014). This can be proven since all nanoparticles presented same absorption profile. This also indicates that the dielectric constants of dispersants not influenced on analysis.

In relation the intensity of the bands, the higher the intensity of absorbance peaks, the better the dispersion and solubility of nanoparticles (Munkhbayar *et al*., 2013; Li *et al*., 2010). The best result of nanoparticles dispersion was found with toluene, convergent with the results of visual analysis. However, nanoparticles dispersed with hexane and ethylene glycol, besides not submit high absorption, it was observed a widening in its plasmon band. This widening occurred by the track of distances between nanoparticles, indicating a particle-particle interaction stronger and cluttered. This suggested a poor distribution of nanoparticles (Persson *et al*., 1983; Otubo *et al*., 2003).

3.2.3 Analysis of the dispersive behavior of nanoparticles after tribological tests

After the tribological test a new analysis by Uv-visible spectrophotometer was realized, as shown in Fig. 4.

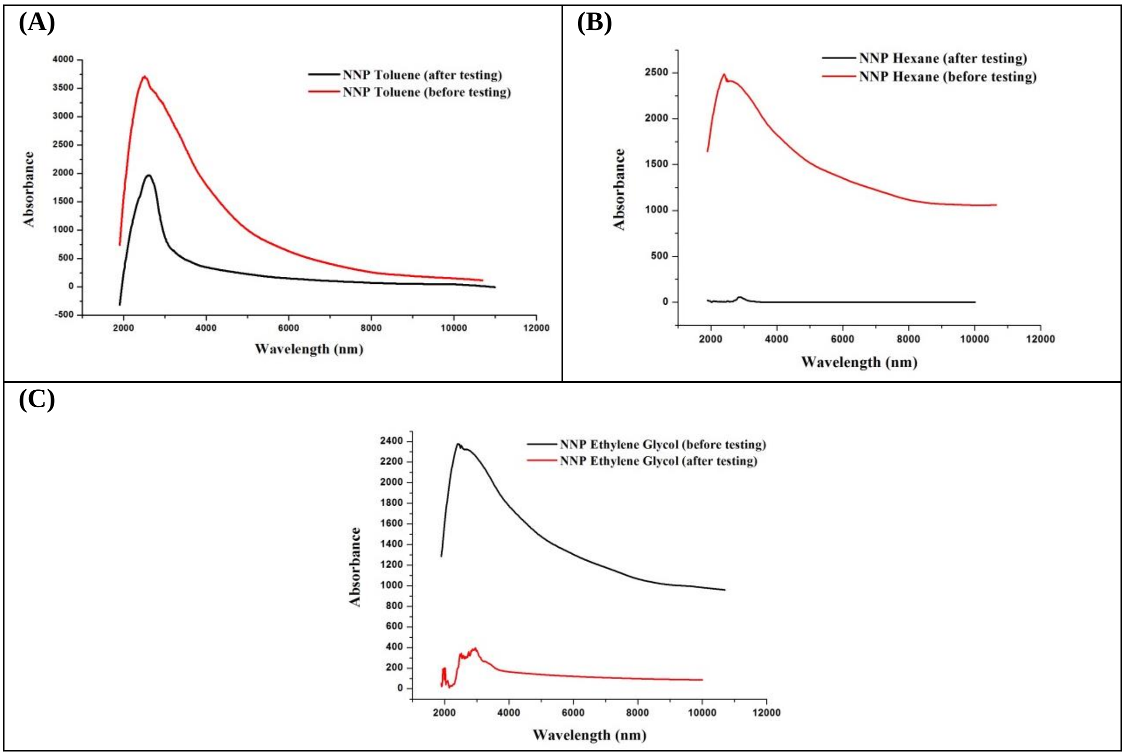

Figure 4. UV–vis absorption spectra: (A) Dispersion in toluene before and after tribological test. (B) Dispersion in hexane before and after tribological test. (C) Dispersion in ethylene glycol before and after tribological test.

The decrease in the intensity of the absorbance peak occurred with all dispersions, since the concentration of the nanoparticles decreased after tribological testing, due to the permanence of nanoparticles on metal surfaces during the test. It is observed in Fig. 4A the dispersion with toluene remained with the largest amount of nanoparticles, only suffering a decrease in the intensity of the peak absorbance, but remaining with a well dispersion. Thus, as the nanoparticles dispersed in toluene remain with a well dispersion and geometry were not modified, the oil can be reused.

The samples dispersed in toluene and hexane remaining with only one plasmon band, in other words, nanoparticles continued with spherical format. The hexane plasmon curve is decrease drastically due the low concentration of nanoparticles in oil after the test and, the minimum remainder concentration still agglomerated, relates to the decrease of intensity plasmon band. Already the sample dispersed in ethylene glycol, as shown in Fig. 4C, presented two plasmon bands, indicating that its geometry has been modified. Nanoparticles dispersed in ethylene glycol whic remain in the oil after the test were damaged passing through the contacting surface, resulting from the exfoliation of nanoparticles and occurring modification of its geometry. This same result was found in the work of Rabaso *et al.*, 2014.

3.3 Evaluation of tribological properties

Figure 5 has the results of the coefficient of friction for the three dispersants, the information of the standard deviations were calculated from the permanent regime. Note that the dispersant exercised direct influence on the coefficient of friction justified by dispersion of the nanoparticles in oil. The variations of the triplicate results also showed to be lower in the dispersed condition in toluene, confirming the results of UV-visible.

According to the results there is a increase in coefficient of friction proportional to poor dispersion or agglomeration of nanoparticles in oil, in the following order: toluene < hexane < ethylene glycol. The same ratio was found for the size of wear scar of balls.

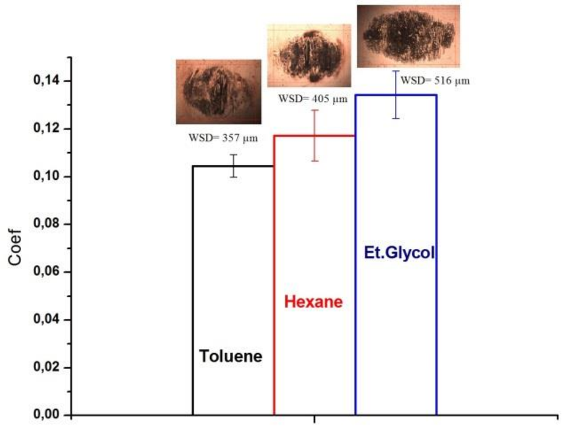

Figure 5. Standard deviation graph of friction coefficient performed in triplicate, with the respective images wear scar balls.

To improve the friction reduction mechanism, nanoparticles adhere on the contact surface, as are smaller or similar size to the thickness of the lubricant film, is deposited on it (Chiñas and Spikes, 2000). Thus, it can happen exfoliation of the nanoparticles on the surface. (Rabaso *et al*., 2014).

Figure 6A friction coefficient behavior shows a response corresponding to film forming in Fig. 6B. As the percentage the film increased, the friction coefficient decreased. Only for ethylene glycol the friction coefficient remained high and constant throughout the test, already the film formation was impaired by the action of nanoparticles. This phenomenon can be explained by mechanisms of action of nanoparticles as a third body, described by Alves *et al*. (2013).

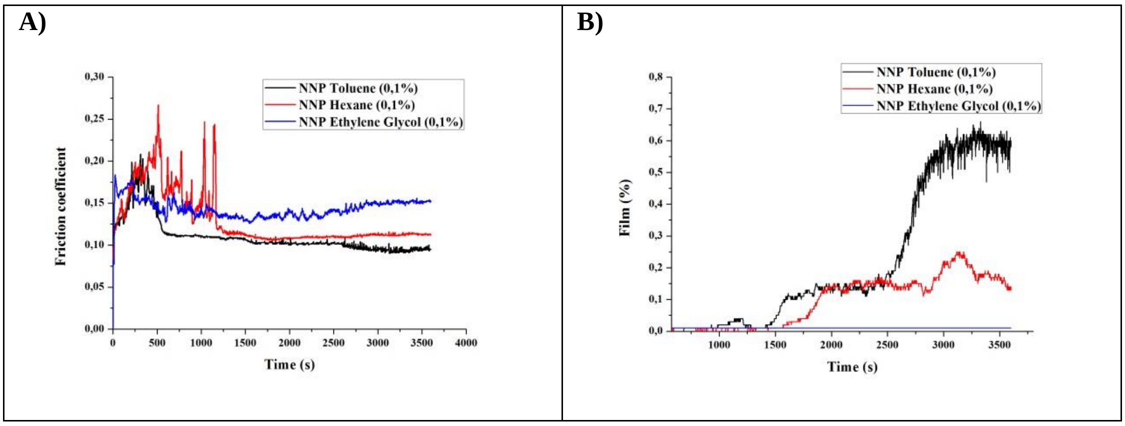

Figure 6. A) Coefficient of friction nanoparticles dispersed in toluene, hexane and ethylene glycol. B) Film Formation of nanoparticles dispersed in toluene, hexane and ethylene glycol from permanent regime.

The deposition of nanoparticles on the surface is directly related to the variation in friction and wear, in this way, the better dispersion of nanoparticles promotes best tribological results (Battez *et al.*, 2008). This can be seen in Fig. 6A and 6B, where the nanoparticles dispersed in toluene obtained the best result of friction coefficient and film formation, consistent with the dispersion results discussed above. Probably nanoparticles dispersed in toluene because they are better dispersed, may carry a proportion of load and separate the two surfaces, improving the friction reducing and wear properties (Jatti and Singh et al., 2015). In the case of dispersions in hexane, its friction coefficient was higher during the test than toluene, probably the lubricating film was partially broken due to poor dispersion of nanoparticles (Yu et al., 2008).

4. CONCLUSIONS

On the basis of results presented above, it can be concluded that:

- Besides the parameters already discussed in the literature for the performance of nanoparticles as additives for lubricants (size, concentration, composition and shape), it is also important to analyze the dispersion of these nanoparticles in the oil, and the effect of using a dispersant to improve it.

- The results of visual dispersion/uv-visible and tribological performance converge in the following order of increasing friction coefficient regarding the use of dispersants studied: toluene < Hexane < ethylene glycoll.
- The analysis of uv-visible before and after the tribological test shows that nanoparticles dispersed in toluene does not suffer changes in the geometry, as well as there is no relevant change in their dispersion.
- Nanoparticles dispersed in toluene can be reused even after tribological test.

5. ACKNOWLEDGEMENTS

The authors wish to express thanks to the LAMEN, Analytics Chemical and Tribology laboratories of UFRN by the availability of equipment for test.

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