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EFFECT NANOOXIDE CONCENTRATION AND DISPERSANT AGENT IN LUBRICANTS ON WEAR REDUCTION

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Abstract. *The use of nanooxides as an antiwear additive in lubricant has been studied by several researches because they exhibit ability to reduce the friction between metal surfaces. However, for an improvement of their performance is still necessary the knowledge and control of some parameters in order to promote a good compatibility with the oil and, consequently, friction reduction. For this purpose, elements that aid in the dispersion of nanooxides in oil need be investigated such as the best nano oxides concentration, once these parameters influence in wear reduction. The aim of this study was to evaluate the effect of the concentration of copper oxide nanoparticles dispersed in commercial synthetic oil, using different types of dispersants agents (toluene, hexane and ethylene glycol) on tribologial performance of lubricant oil. The contact tests were carried out in tribometer HFRR with maximum load conditions. The better antiwear action was observed for the oil with 0.1% of nanoparticles for all dispersants. Also, in terms of dispersant agent, the Toluene showed lower coefficients of friction.*

Keywords: *Nanoparticles (NNP), concentration, dispersant, friction coefficient.*

1. INTRODUCTION

The application of nanomaterials has gained interest in many research areas, and recently it has been identified its potential in the development of high-performance lubricant when used as anti-wear additives reported in the work of Viesca et al (2011), Trajano (2013) , Yy Wu (2007) and Martins et al (2013).

Oxides nanoparticles have demonstrated antiwear action when added to lubricating oils; this occurs due the action mechanism that exercise on the contact surfaces. Several authors have studied the friction reduction oxides effect, such as Battez et al. (2005) investigated ZnO, Li et al. (2010) the ZrO2 / SiO2, Viesca et al. (2011) and Yu et al. (2008) investigated the CuO applications as antiwear additives. These oxides are interesting, because they are not harmful to the environment, differently of other commercial additives commonly used for this function.

The copper nanooxide has potential due its crystalline structure and chemical nature, which allow a direct function in the protective films formation (Zin et. al, 2014). However, for use of nanoparticles in lubricants there needs to be a control of some parameters before the additivation, because the reduction of friction and wear are dependent on characteristics of size, form and concentration of nanoparticles (Wu et al., 2007).The control of nanoparticles concentration has great importance because if they are in excess, they can act negatively. In their studies, Wu et al. (2011) identified that a low concentration from 0.05 to 2.97%.w is sufficient to improve the tribological properties of the lubricants. However, even working at low concentrations, a problem related to the use of metallic nanoparticles have been reported, attributed to their agglomeration facility (Dong et al., 2014).

In order to minimize the agglomeration of these nanoparticles, it is necessary to use substances that aid oil dispersion. Commonly an organic solvent, soluble in oil is used as the dispersant. Laurent et.al. (2008) found good dispersion of magnetite nanoparticles with toluene and hexane; Wu and Kao (2011) dispersed TiO_2 nanoparticles in ethylene glycol lubricants to reduce aggregation of the particles after preparation.

Thus, this work aimed to evaluate the effect of copper oxide nanoparticles concentration added in PAO in antiwear action when using different dispersants (toluene, hexane and ethylene glycol) in high contact pressures.

2. EXPERIMENTAL AND METHODS

2.1. Synthesis and Characterization of Nanoparticles

The synthesis of nanoparticles occurred from the preparation of two solutions: one solution of copper acetate, in which were dissolved 2 mmol monohydrate acetate of copper in 40 ml of ethanol; and an alcoholic solution of sodium hydroxide, being 8 mmol of NaOH dissolved in 40 ml of ethanol with the same stoichiometric ratio. 10 ml of each solution were put a Teflon reactor and carried out to the microwave (Panasonic NN562BK) with a power of 99 Watts by 140 s, pulse on / off 20s and 10s, repeated nine times of this process, in order to maintain the mixture at an average temperature of 80 ° C. After this process, the reactor was cooled by 5 min at 15 °C and the solution was recovered by centrifugation for 5 min. Finally, the nanoparticles were washed with warm water and ethanol and after centrifuged. They were dried at 60 ° C for 2h or until complete evaporation of the ethanol.

The nanoparticles were coated with 0.01 g of oleic acid and 0.2 g of CuO nanoparticles, added at 20ml of ethanol. The mixture was submitted to magnetic stirring for 2h at 60 ° C; the solution was centrifuged for 10 minutes and dried for two h or until complete evaporation of the ethanol.

The nanoparticles were characterized by X-ray diffraction (XRD) to verify the chemical structure of the particles. The analysis was performed on diffractometer XRD -600- Shimatsu, with the Ka-alpha radiation. The crystallite size was calculated from diffractograms using the Scherrer Equation (Klug et. Al., 1962).

$$Dhkl = k\ \lambda\ /\ ß.\ \cos.\Theta,$$

Where:

- Dhkl is crystallite size;
- k is the form factor of the sphere (0.89);
- Θ angle of diffraction;
- ß half the total width (FWHM) of the peak;
- λ is the wavelength of X-rays (1.54056 A).

2.2. Dispersion of nanoparticles in oil

Organic solvents were used to ensure a better dispersion in oil. The dispersion occurred with three concentrations of nanoparticles and three variations of solvents, as can be seen in Table 1.

Table 1- Fractions of dispersant, oil and nanoparticles.

Dispersing	Concentration of NNP					
	0.1% (0.008g)		0.25% (0.02g)		0.5% (0.04g)	
	Oil	Dispersant	Oil	Dispersant	Oil	Dispersant
Toluene	8mL	2mL	8mL	5mL	8 mL	10mL
Hexane	8mL	0.2mL	8mL	0.2mL	8 mL	0.2mL
Et. Glycol	7.2mL	0.8mL	7.22	0.78mL	7.24 mL	0.76mL

The dispersion was performed by adding nanoparticles in the solvent and after in the oil, stirring the solution at 20 ° C for 6h. Then drying was performed at 70 ° C until complete evaporation of the solvent.

2.3 Tribological test

The tribological test was performed through the use of tribometer HFRR (High Frequency Reciprocating Rig Test). The test consisted of sliding the polished ball (570-750 HV 6.0 mm in diameter) on the disk (AISI 52100 untreated, 190-210 HV 10mm in diameter and Ra ≈0.0067μm) with test parameters: course of sliding 1.00 ± 0.02 (20 ± 1 Hz) under lubricant action with 2mL of oil, temperature of 50 ° C, normal load of 10 ± 0.01N and duration 60 min. The tests were performed in triplicate. After the tribological test, the worn surfaces of the tribological pair was assessed visually in light microscope Olympus CX21FS1.

3. RESULTS AND DISCUSSION

Fig.1 shows the patterns of X-ray diffraction of the synthesized nanoparticles. The diffractograms obtained suggest a formation of cupric oxide - CuO, by peaks with angulation of 38.44 °, in agreeing to the limits which characterize it

35.7 to 38.5 ° (Urquieta-González et al., 2002). From the diffractograms it is also possible to obtain the average crystallite size by the Scherrer equation, which was 5.5nm, the results agreeing Medeiros et al. (2014). It was also observed the formation of a single phase with high purity and crystallinity due to the application of microwaves as described by Jamil et al. (2008) and Rybakov et al. (2008).

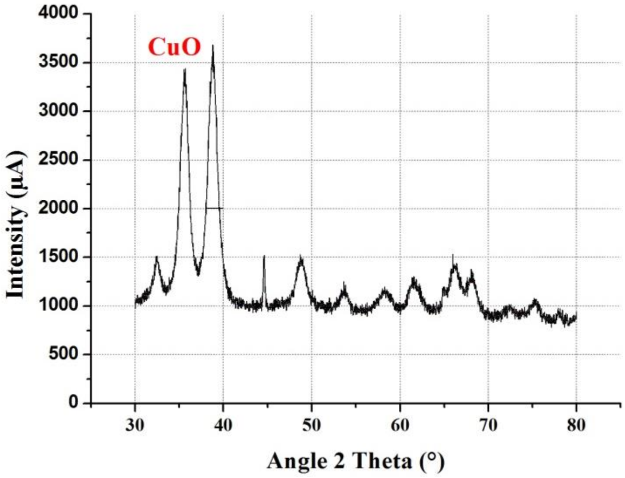

Figure 1- XRD pattern of copper oxide.

Figure 2 shows the results of friction coefficient by the HFRR tribological test with pure oil (PAO) and added of 0.1% of CuO nanoparticles dispersed in toluene, ethylene glycol and hexane. The film formation during the test took place after breaking the support of debris (running-in stage) when the ball comes into contact with the disk, and the highest peaks are broken. This running-in time was smaller for oil with toluene dispersion around 570s, while for the hexane it was 1100s and ethylene glycol 600s, indicating which began the lubricant film formation. The running-in stage finished faster for toluene indicating that the particles in dispersion were better distributed, and this suspension was more stable, facilitating the film formation. According Chen and Liu, (2001), inorganic nanoparticles are not suitable for lubricating oils because they have poor disperse capacity. However, the use of dispersant improves this dispersion.

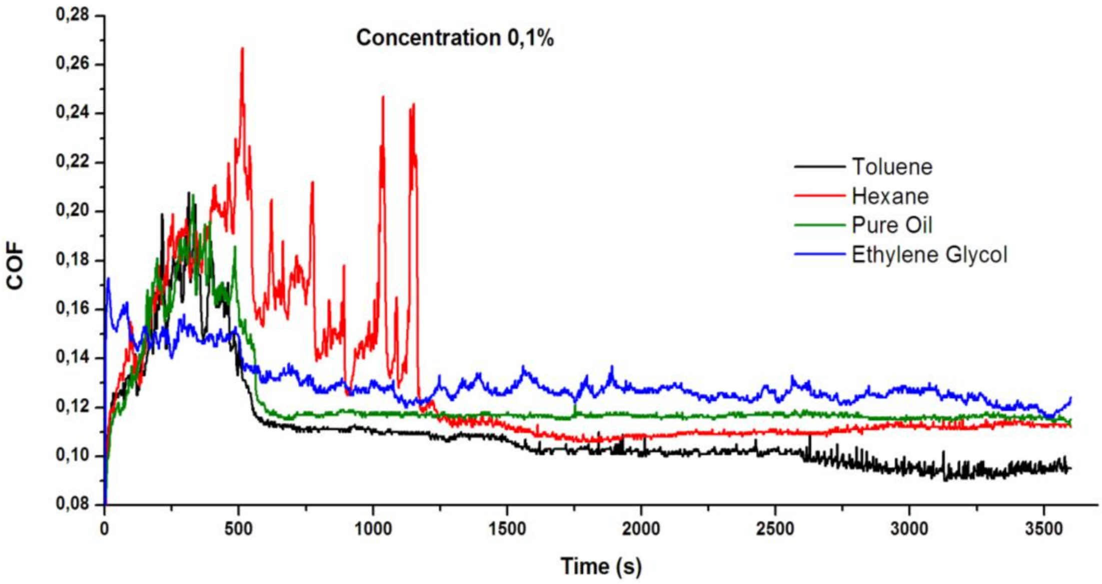

Figure 2 - Friction coefficient of additivated oils with 0.1% NPN CuO.

In Fig 2 shows changes in action mechanisms of nanoparticles during some tests. These mechanisms described by Peng et al. (2009) are: smaller nanoparticles are likely to interact with the contact surface forming a protective film; small nanoparticles are likely to roll between the contact surfaces changing the rolling friction for rolling and sliding;

the compressive stress concentrations combined with high pressure can be reduced by supporting offered by nanoparticles; and nanoparticles are deposited forming the physical tribofilm.

The toluene dispersion is observed after 600s where is decreased in the friction coefficient attributed the started the lubricant film formation. From 600s is formed a lubricant film and the nanoparticles act by the effect of the smoothing surface, micro-grooves are formed, become smoother. Increase of testing time (1500-2500s), then more spherical CuO nanoparticles are rolled into contact area as tiny ball bearing so that the sliding friction decreases gradually to 2500s, this mechanism was found for Peng et al. (2009). After the 2500s occurs more friction reduction due the next mechanism action of nanoparticles, described by Chiñas-Castilho and Spikes (2000) when the nanoparticles do indeed penetrate the rolling contacts to form patchy films at low speeds, colloids formed a boundary film of at least one or two times the particle size.

For dispersion with Hexane, the running-in stage occurred with higher maximum coefficients of friction, this probably happened to poor distribution of nanoparticles in the oil causing them to take longer on accommodating the contact surface and act. For this case, it was observed the first two mechanisms presented in toluene, and the smoother surface of the 1270s until 1530s, and the rolling of 1530 until the 1930s. From this time nanoparticles stopped acting, with only the lubricant film formation acts, resembling the pure oil. A hypothesis to explain this fact is the poor distribution nano-oxides in oil.

As for the dispersion with ethylene glycol running in stage was not as high, having the same tracks that pure oil and toluene , but throughout the test, the friction coefficient remained high compared to other dispersants due to poor dispersion provided by ethylene glycol. In this case, when CuO nanoparticles were added, they present behavior of a third body increasing the friction coefficient, as occurred in Alves et al (2013) work.

Figure 3 shows the friction coefficients for oils additived with CuO 0.25% dispersed with the same solvents already mentioned.

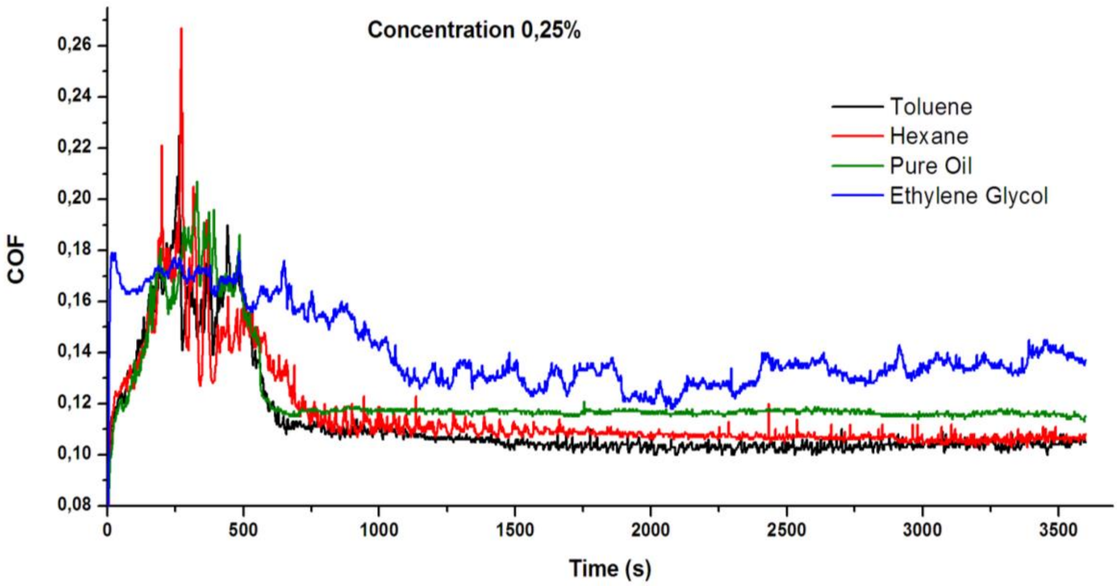

Figure 3 - Friction coefficient for additived oils with 0.25% NNP of CuO.

The results observed for this concentration were similar to the previous. There was a small increase in running-in stage time for all concentrations, and the film formation occurred from for 600s for toluene, 750s hexane and 1150s to ethylene glycol. This was due to a higher concentration of nanoparticles because they require a longer time for accommodation.

For sample dispersed in toluene were observed the same mechanisms actuation for the concentration 0.1%, only noting the delay in the transition of these mechanisms.

At a concentration of 0.25% in oil dispersed with hexane showed a decreased coefficient of friction, with behavior similar to toluene in the concentration of 0.25%. A fact to be emphasized is the formation of tribofilm observed in 3000s, which did not occur in 0.1%. In concentrations of 0.1% there were a smaller amount of well dispersed particles in oil, different from what occurred for this concentration which there are more particles to be dispersed, so that there was a proper deposition of CuO on the contact surface. The hexane under this condition has good performance being a good alternative to having smaller toxicity than toluene.

Already ethylene glycol showed similar results of 0.1%, showing coefficient values larger than the previous one; this is because their greater amount of agglomerated nanoparticles.

Figure 4 presents the friction coefficients to NNP concentration of 0.5% for variations the dispersants.

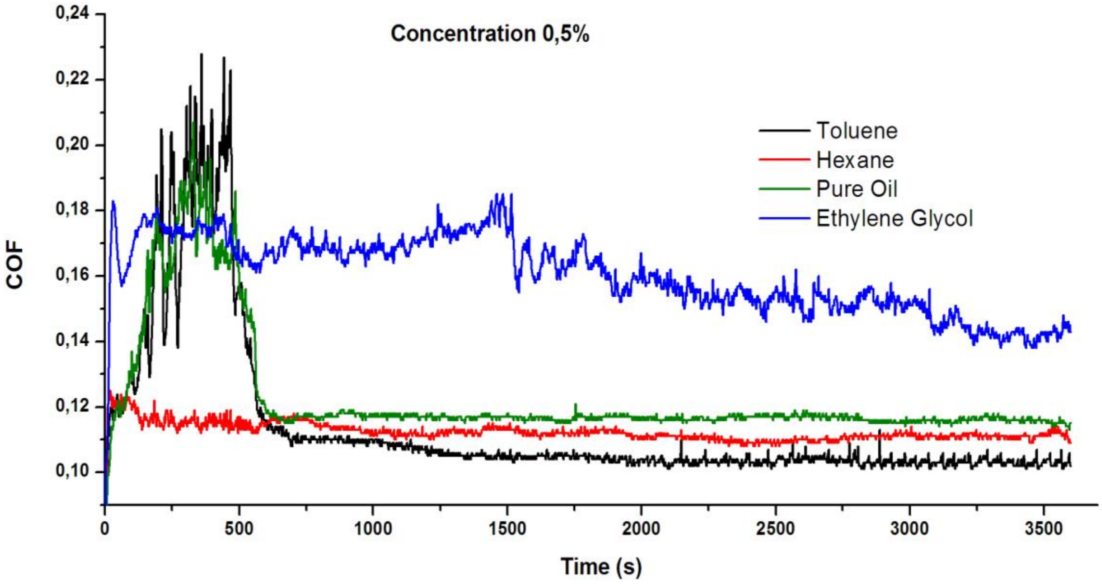

Figure 4 - Friction coefficients for NNP concentration of 0.5% CuO.

For the concentration 0.5% and dispersing in toluene the nanoparticles may have been confused with the asperities contact increasing the maximum friction coefficient during running-in stage entailed in the smoothing surface, with the same time intervals. After the 2100s the acting mechanism until the end of the test was rolling, not being observed the formation of tribofilm.

Already hexane showed a decrease of maximum friction coefficient values in running-in stage, with coefficients similar to toluene. The reduction of the friction coefficient can be associated with smoothing surface action by nanoparticles. The rolling mechanism of the nanoparticles was observed in the range 2300 until 2700s.

Under these conditions, the ethylene glycol had the highest coefficients of friction, with an increase of 33% compared to the pure oil having the same predominant mechanism action of the first two concentrations.

Among the results shown it can be seen better performance for concentrations of 0.1% nanoparticles, as well as in the work of Li et al (2010), in which the average friction was reduced when used in concentrations of 0.1% by weight nanoparticles, they entered the zone of contact and sliding on the surface resulting in decreased friction.

When added copper nano oxides (with minimal scattering) the pure oil, there is a reduction of the friction coefficient, as was found in the work of YU et al. (2008) that added CuO nanoparticles.

Figure 5 shows the average friction coefficients for all concentrations and all the dispersants used in the permanent regime.

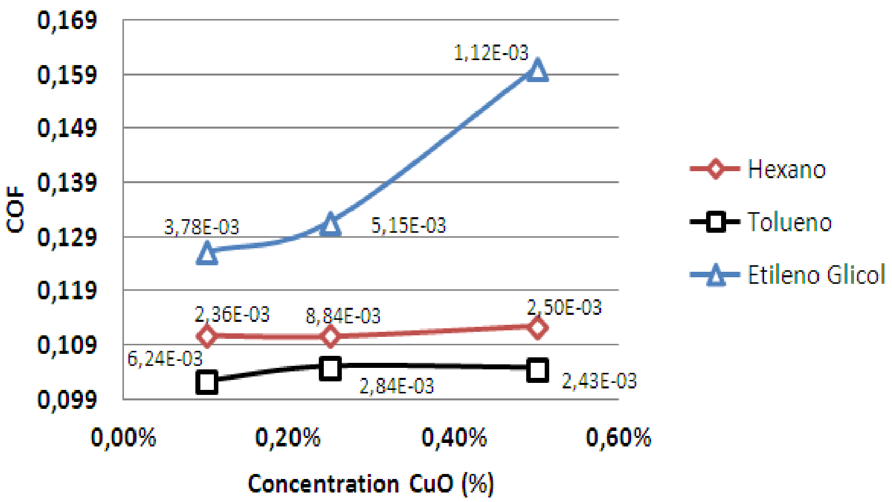

Figure 5 - Friction coefficient Average for additives oils with CuO and dispersed in toluene, hexane and ethylene glycol in the permanent regime.

The results presented in Figure 5 demonstrate the proper dispersion when using toluene, which guarantees a good deposition of the nanoparticles and promoting an action on the entire surface of the material reducing the friction. The use of hexane also results in a considerable dispersion, since this reduces the coefficient of friction, and it is less toxic than toluene. The use of such dispersant agrees with Laurent work et.al. (2008) that found good dispersion of magnetite nanoparticles with the use of toluene and hexane.

Wu and Kao (2011) dispersed TiO2 nanoparticles in ethylene glycol lubricants to reduce the aggregation of particles after preparation. However, in the copper oxide use, the ethylene glycol does not promote a good dispersing nanoparticles, increasing the coefficient of friction, even profile already demonstrated in this study.

Tables 2 and 3 show the average sizes relating to the wear on the disc and ball after tribological testing, and Figures 6, 7 and 8 present the wear on the disc with the use of dispersants, respectively observed by microscopy.

Table 2 - Average size of scars on the discs after testing (in microns). Measured by average between length and width the wear.

	Toluene	Hexane	Ethylene Glycol
0.10%	900.38	733.85	1005
0.25%	906.1	923.5	789.17
0.50%	930.96	756.5	977.58

Table 3 - Average size of scars on the spheres after testing (in microns).

	Toluene	Hexane	Ethylene Glycol
0.1%	356	405	380.5
0.25%	363	379	431.5
0.5%	388	270	564.5

The images in optical microscopy do not offer enough focal quality due to equipment limitations. However, through them can see that the wear was more severely in the center of the disc, this may be attributable the reciprocating movement of the test configuration. The migration of nanoparticles to the edge can explain the smaller wear in this region.

Also, it is possible to observe that by increasing the concentration of the nanoparticles was increased the wear to all the dispersants, confirming the behavior of the coefficient of friction. Assessing the average sizes of the discs and ball scars, with use of toluene, the wear increase is proportional to the concentration of NPN, as occurred for ethylene glycol, because the rise of concentration potentiated the wear. The other hand for the hexane, the scars on the ball were decreased with concentration. However, it should take into consideration the friction coefficient and wear depth for this condition in the disc, that was higher than dispersed in toluene, showing that only the observation of wear in the scars is not conclusive.

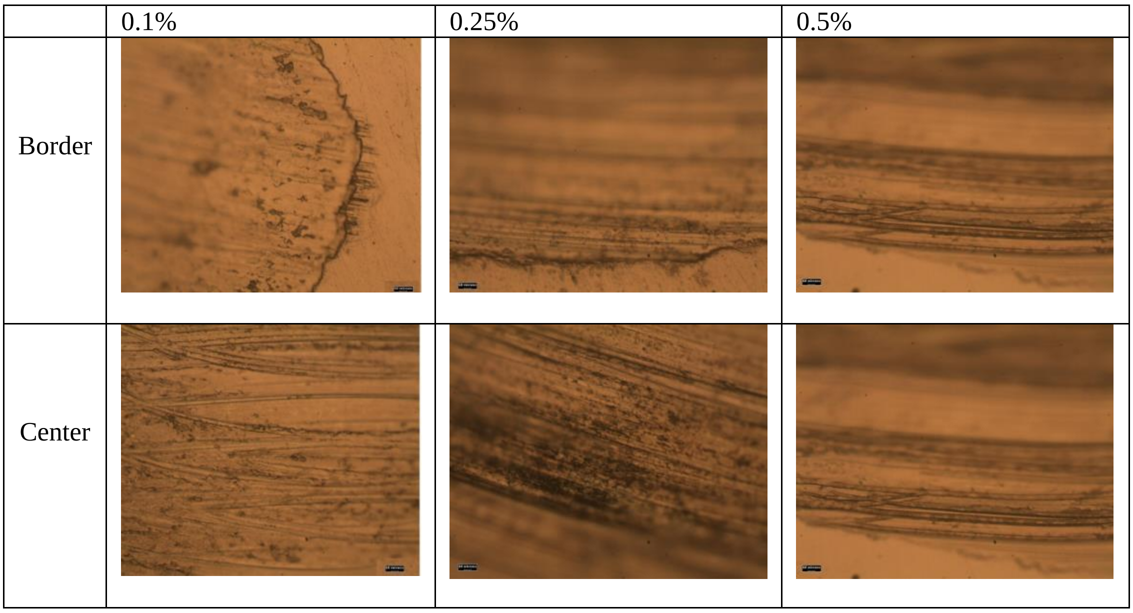

Figure 6 - Discs after testing with the use of ethylene glycol dispersant.

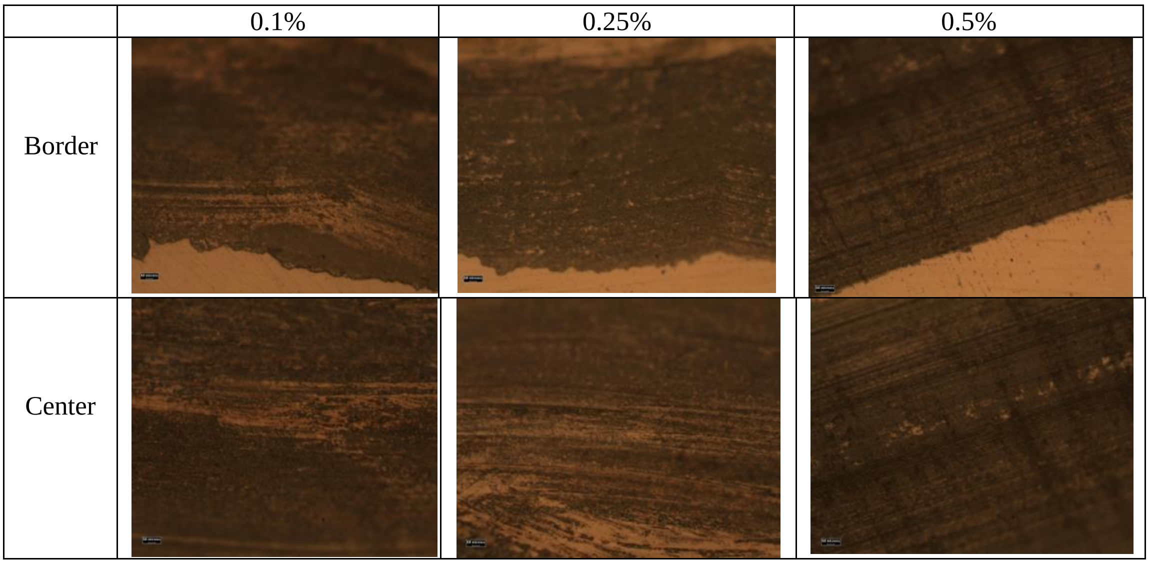

Figure 7 - Discs after testing with the use of to hexane dispersant.

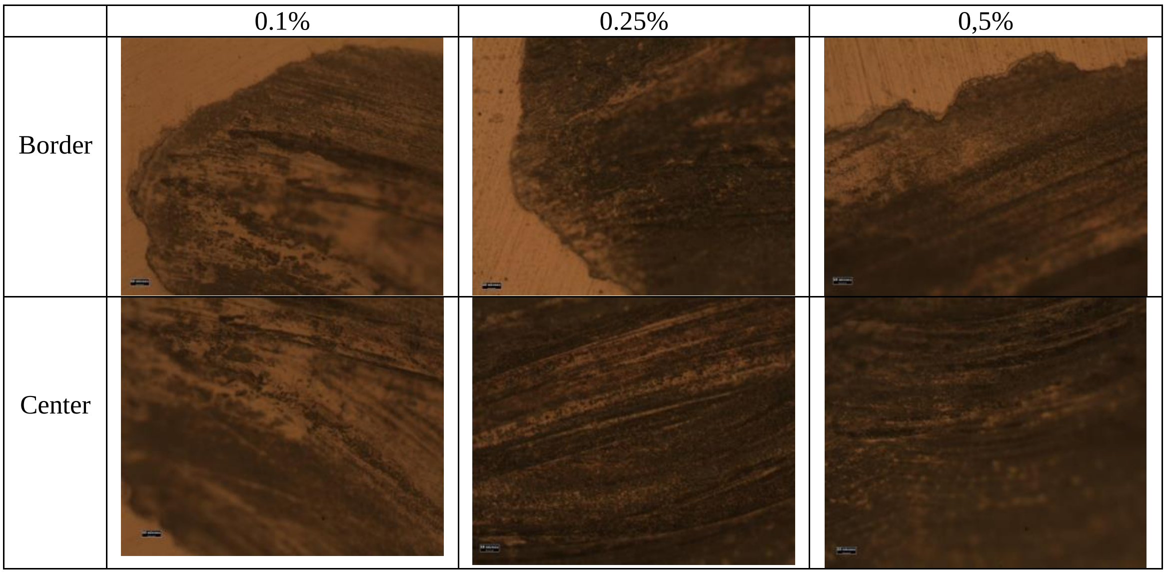

Figure 8 - Discs after testing with the use of toluene dispersant.

4. CONCLUSIONS

Through the tests performed it can be concluded:

- Addition of CuO nanoparticles dispersed in toluene and hexane reduce the coefficient of friction;
- Toluene showed better dispersion than the other solvents in all the concentrations, with improved performance at low amount of nanoparticles;
- The hexane showed better performance in low concentration conditions, resembling the toluene in the concentration of 0.25%, having, however, lower toxicity;
- Ethylene glycol did not help in proper dispersion of nanoparticles, increasing the wear;
- The friction coefficient was proportional to the concentration of NNP for ethylene glycol and toluene;
- It was possible to reduce the coefficient of friction under the conditions of minimum NPN concentrations when they are well dispersed.

5. ACKNOWLEDGEMENTS

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