INTRODUCTION

Nanoparticles when suspended in a lubricant can infiltrate small gaps between rough surfaces in contact and alter the contact's tribological performance. Hence, nanoparticles offer an alternative approach to lubrication by introducing third body entities directly into the contact. The ability of nano-sized particles to pass through conventional filters, penetrate into contacts that larger particles cannot, along with the enhanced scale dependent properties of the nano-sized particles have made them a promising new type of lubricant additive. Different nanoparticles have proven to reduce the coefficient of friction in base oils up to 25% and 50% in recent studies [1-3]. The dominant enhancing mechanisms of nanoparticles are uncertain or unknown with few exceptions (such as for film forming particles). All of the proposed mechanisms for nanoparticles such as rolling [4], transfer films [1], formation of tribofilms [5], polishing [6] and reducing the real area of contact [2, 7] would justify the friction reduction induced by the nanoparticles. However, a physical understanding that explains the synergic effect of these mechanisms and the effect of nanoparticles on wear is yet to be formalized. Furthermore, the interaction of nanoparticles with base oil and additive package components is not yet fully understood. These are the missing links in our understanding of the nano-lubricants and hinders the industrialization of nano-lubricants in major applications. This work utilized strategically designed experimental analyses to evaluate the role of nanoparticles in wear and the effect of nanoparticles on wear is yet to be formalized. Furthermore, the interaction of nanoparticles with base oil and additive package components is not yet fully understood. These are the missing links in our understanding of the nano-lubricants and hinders the industrialization of nano-lubricants in major applications.
nanoparticles used in this work can be obtained in and out of solution without any chemical interventions. Therefore, these particles are an ideal candidate to perform dry friction tests to understand the explicit role of nanoparticles in contact.

2. **Base lubricant's effect.** In these experiments CuO particles are suspended in (i) dodecane, (ii) polyalphaolefin (PAO) base oil and (iii) fully formulated SAE 5W20 engine oil. The friction experiments on nano-lubricants with the same type and concentration of nanoparticles can reveal the role of surface-to-surface interactions in the system.

The CuO nanoparticles are coated with sodium oleate, are on average 11 nm in diameter and are prepared in a chloroform solution according to [8]. The solution was applied on the surfaces and dried using a heating lamp. This would leave dry CuO particles in powder form on the surface for dry tests. Moreover, the same solution can be used to make the nano-lubricants. This was done by applying the CuO-chloroform solution to the base lubricant and evaporating the chloroform using heat and vacuum while stirring the solution. All the CuO nano-lubricants were prepared at a concentration of 5.0%wt of CuO particles to highlight the particles' effect in the experiments. It should be noted that this is a very high concentration of nanoparticles, which is far from the optimum concentration for reducing friction and wear. This relatively high concentration was chosen for the purpose of intensifying the nanoparticle to surface interaction effect in the test. The CuO nano-lubricant in fully formulated SAE 5W20 oil is also prepared as mentioned above and also consists of 5.0%wt of CuO nanoparticles coated with sodium oleate.

**RESULTS**

The experiments were carried out using the pin-on-disk and disk-on-disk methods. Figure 1 shows the coefficient of friction (COF) versus time for the CuO nanoparticles dry test in comparison to the control test. It should be noted that the tests were done by a pin-on-disk setup with a 1 Hz frequency. Therefore the time axis is also the cycle axis in these tests. Figure 1 shows the results for a normal load of 2.0 N. In this test the dry CuO nanoparticles reduce the COF significantly in the first 400 cycles. However the COF then increases to the value of the control after 400 cycles.

The hypothesis was that the nanoparticles are pushed out of contact during the test and that is why there is an increase in the COF signal.

In order to prove that the performance of the particles on the surface is solely governed by their concentration, another dry test was run. In this experiment the nanoparticles were deposited on the surface in powder form and the test was run at a normal load of 2.0 N. As was expected, the dry CuO particles stopped reducing the COF at about 400 cycles (see Figure 2).

However, this time the test was stopped and dry CuO nanoparticles were reapplied to the surface to account for the decrease in COF signal. Figure 2 shows the COF for the test stopped when the nanoparticles stopped performing to add particles to the contact and resume the experiment.
for the particles pushed out of the contact zone. The test was resumed, and as the results show in Figure 2, the particles decreased the COF for another 400 cycles. Afterwards, the COF began increasing again. This time the test was stopped and a small portion of the nanoparticles in the pile-up around the edges of the contact were pushed back into contact zone. The test was resumed and it was observed that a small amount of the particles could decrease the COF again. This test proved that the reduction of the nanoparticles concentration in the contact zone is responsible for the increase in friction. More tests with different normal loads and also on a disk-on-disk setup were performed (results not presented here) to further verify this phenomenon.

There is another major observation to be made here—there is a critical concentration of the nanoparticles, below which the nanoparticles can’t decrease friction. In other words, as the nanoparticle content is being reduced as the test progresses (Figures 1 and 2) the COF seems to be fairly constant until it reaches a certain point. Beyond this point the nanoparticles can’t decrease the COF anymore and the COF begins increasing rapidly until it reaches the control’s value. In order to measure this critical concentration a test was stopped right before the particles stop performing. An XPS analysis was performed inside the contact zone to measure the stoichiometry of the elements on the surface. The measurement showed that there is 1.6 at% of Cu on the surface right before the particles stop performing (see Figure 3). The XPS analysis on the control sample did not show any trace of Cu element. Additionally, surfaces were drilled a depth of 12.5 nm using Ar sputter cleaning. Analysis of the drilled surface didn’t show any trace of Cu, which means that Cu is strictly present on the surface only.

The next round of experiments were done using the CuO particles in various base lubricants and different normal loads. Friction tests were performed and wear measurements were carried out using the three-dimensional surface profile, as shown in Figure 4. The results for normal load of 20 N are presented in Figure 5 and show that the CuO particles when suspended in dodecane can reduce both friction and wear significantly.

In the case of PAO base oil, it is observed that the control PAO marginally outperforms the nanolubricant at a normal load of 20 N (see Figure 5). However, when the test was repeated at a higher normal load of F=50 N, the nano-lubricant yields a lower COF value (see Figure 6). This shows that the performance of the CuO particle in PAO depends on the normal force. The particles are increasing friction at a lower normal load of F=20 N while they decrease friction at F=50 N. A possible explanation is that at higher loads there is a higher possibility of particles engaging in contact. The effect of particles on wear is also mixed and the experiments do not produce a clear trend.

Next, a set of experiments were conducted that focused on the effect of CuO nanoparticle additives on fully formulated SAE 5W20. The friction tests were performed at normal loads of 20, 50 and 150 N. The friction and wear results are presented in Figures 5 and 6. CuO particles are observed to consistently increase the COF when added to the formulated oil (this is due to the high concentration of the particles that was used in this test). However the effect of nanoparticles on wear is mixed and varies with the normal load. At the lower loads of 20 and 50 N the nanoparticles were
capable of reducing the wear (Figure 5). However, when the load was increased to 150 N, nanoparticles had a negative effect on wear (Figure 6). At higher loads, the film forming additives of the 5W20 are more active. In addition, nanoparticles are more inclined to abrade the contact surfaces at higher loads. In order to investigate this, additional surface analysis was performed on samples tested with 5W20 at a normal load of 150 N. The results (not presented here) showed that the presence of the particles in high concentrations can interfere with the formation of tribofilms.

DISCUSSION

In a previous study on CuO nanoparticles [2], it was suggested that the nanoparticles engage in contact between the surfaces and reduce the real area of contact between the surfaces. However, it was observed that particles can abrade the surfaces based on their concentration. In order to further assess this mechanism a follow up work developed a contact model for nanoparticles in between rough surfaces [7]. The model was able to verify the reduction of the area of contact as a key mechanism associated with the performance of nano-lubricants. The current work is a continuation of the study with a focus on the synergistic effect of the area of contact reduction mechanism with other proposed mechanisms for nanoparticles.

The dry friction tests using the CuO particles offered some key observations. The most important was that there is a critical concentration of nanoparticles, below which the particles can’t sustain a reduced COF. The dry friction test offers a methodology to measure this critical value. From a practical stand point this means that the particle concentration in the nano-lubricant should be such that this critical amount is fed into the contact zone. Also, the reduced COF value was observed to not be directly related to the nanoparticle content in contact as long as the concentration is above the critical value.

The tests on dry CuO and CuO solution in dodecane, PAO and 5W20 showed some interesting trends. The particles are more effective at reducing friction and wear when suspended in an inferior lubricant or in a dry form. The particle’s effect on PAO base oil is dependent on the normal force (contact pressure) and is desired at higher loads. The particle’s effect on fully formulated SAE 5W20 is also dependent on the normal force (contact pressure). All things considered, it is as if the CuO particles exhibit competing effects on a contact’s tribology. The effect of CuO particles exists in two forms: (i) abrasive interaction with the surfaces and (ii) reduction in the area of contact. The schematic of different effects of particles is shown in Figure 7. Particles create voids that reduce the real area of contact. In addition, the particle’s lateral or shear interaction with the surface also affect the contact’s tribology. In case of CuO particles, it is an abrasive interaction with the surface. Both of these interactions affect the overall friction and wear in the system. The overall friction in the system has two components, the friction force as the result of surface-to-surface interaction and the friction force as the result of particle-to-surface interaction, which in equation form is Eq. (1).

\[ F_{overall} = F_{surface} + F_{particle} \]  \hspace{1cm} (1)

The \( F_{surface} \) can be rewritten as \( A \tau \) so that is the area of contact between the surfaces times the average shear stress between the surface. Substituting this into Eq. (1) yields the overall friction as shown in Eq. (2).

\[ F_{overall} = A \tau + F_{particle} \]  \hspace{1cm} (2)
The CuO particles affect both of the friction components. They directly induce a friction force by scratching the surface, $F_{\text{particle}}$. They also affect the friction force between the surfaces by reducing the area of contact, $A_s$. These two effects are competing and one can dominate the system depending on the normal force, the lubricant type ($\tau_s$) and the particle content. In the case of dry tests or inferior lubricants, $\tau_s$ is so large that the first term dominates the equation and the friction induced by the particles is negligible. That is why the only effect that can be seen is the positive effect of the particles on the area of contact. Hence, the results are in agreement with the reduction in the area of contact mechanism. However when a superior lubricant is used, such as the PAO, both of the terms contribute to the overall friction. Then the results are mixed, less decisive and dependent on the conditions. Similar arguments stand for the effect of nanoparticles on wear.

Expanding this discussion to the other types of nanoparticle additives, one can say nanoparticle additives have a dual effect on the tribology of contact. They have a direct effect defined by the interaction between the particles with the surfaces. This effect could be plowing, deposition of transfer films or rolling (see Figure 7). This interaction is dependent on the character of the individual particles. The particles also have an indirect effect caused by the nanoparticles reducing the real area of contact between the surfaces. It might be possible to control the area of contact and tune the effect of the lubricant on the system. This is more of a general effect induced by particles on the contact. The overall effect of the nanoparticle additives on friction and wear is determined by adding the two effects together. This explains some of the common contradictions in the nanoparticle research, such as why hard particles can decrease wear. That is because the reduction in wear is the result of the particles indirect effect on the area of contact.

Another contradiction is why some nanoparticles can reduce or increase the COF depending on the base oil. That is because particles when suspended in an inferior lubricant can better influence the contact tribology through the indirect effect. Whereas, in case of a superior lubricant the particle’s direct effect may overshadow that.

**CONCLUSION**

In this work strategically designed experiments were used to investigate the role of nanoparticles in a contact’s tribology and the effect of nanoparticles on fully formulated oils. The experiments were run using the dry CuO particles powder form and CuO particles suspended in dodecane, PAO and SAE 5W20 oil.

The dry experiments showed that the nanoparticles even absent of the lubricants can reduce both friction and wear. The behavior of the dry nanoparticles was in agreement with the reduction in the contact area mechanism. The dry experiments also presented a practical way of measuring the critical concentration of particles below, which particles can’t maintain a reduced COF. The studies on the effect of CuO particles in dodecane and PAO suggested that the particles have a dual effect on the contact’s tribology. CuO particles can affect the tribology through direct interaction with the surfaces or by reducing the area of contact. This is why the nanoparticle effectiveness depends on the type of the lubricant and the normal load.

**REFERENCES**


