USE OF NANOTECHNOLOGY IN THE LUBRICANTS INDUSTRY

ABSTRACT

This paper aims at highlighting the use of nanotechnology in lubricant additives to the field of lubrication experts, emphasizing the importance of additive chemistry in applied science. It provides initial guidance on nano-additive mechanisms in various lubricants. When added to a base oil or water, nanoparticles may enhance various tribological properties, such as anti-friction, anti-wear, extreme pressure, flash point and high temperature resistance. However, not all submicron particles have the same properties, and as a result, not the same benefits. The goal of this paper is to investigate the chemistry, morphology, and characteristics of different types of nanoparticles and examine the mechanisms of their interaction with contact surfaces in water-based solvent and oil formulations.

Introduction

Humanity's quest for energy is as old as the human race itself. The control of fire, for instance, was a turning point in technological evolution; it acted as a catalyst for the development of advanced civilization. Over thousands of years, we have shifted our focus from merely obtaining energy to now controlling it and reducing energy consumption. With the understanding that our current sources of energy are finite, the scientific world is now more concerned with energy efficiency and alternative energy resources. As such, it has become increasingly important to identify and reduce mechanisms of energy loss. One of the most common causes of energy loss today is friction. In fact, over 25 percent of global energy is lost due to friction and wear in a variety of different processes and applications [1]. In the world of tribology specifically, researchers are keen on developing high performance greases and lubricants to counter the effects of friction in both consumer and industrial applications.

With the ever-increasing demand for more robust, efficient, and environmentally friendly lubricant solutions, consumer industries have begun exploring the implementation of nanomaterials in their products. Nanomaterials have been slowly replacing many traditional chemicals across several different industries over the past few decades, as they provide superior physical and chemical properties due to their high surface area to volume ratio. The grease and lubricants industries are especially keen on investing into nanomaterial research as the use of nanoparticles drastically increases lubricant performance, longevity, and durability. By the year 2025, it is estimated that the market size for automotive, marine, industrial, and aerospace lubricants will be valued at over $166 billion [2]. As such, companies around the world are driven to develop superior products.

Background

Ancient Egyptians were one the first civilizations to encounter and solve this friction problem while building the pyramids. As shown in this wall painting from the tomb of Djehutihotep in Fig. 1 below, dozens of workers can be seen pulling sleds in order to carry a statue to a building site [3]. Also shown in the image are people pouring some sort of substance on the ground just ahead of the sled.

It is unclear, however, what substance the Egyptians used in the process. It is speculated that water or some type of oil could have been used. In any case, by wetting the sand ahead of the sled, the workers had significantly reduced the friction between the sled and the sandy ground, saving time and energy in their transportation efforts.

One of the earliest researchers of the friction phenomena was Leonardo Da Vinci. From the late 1400s to early 1500s, Da Vinci

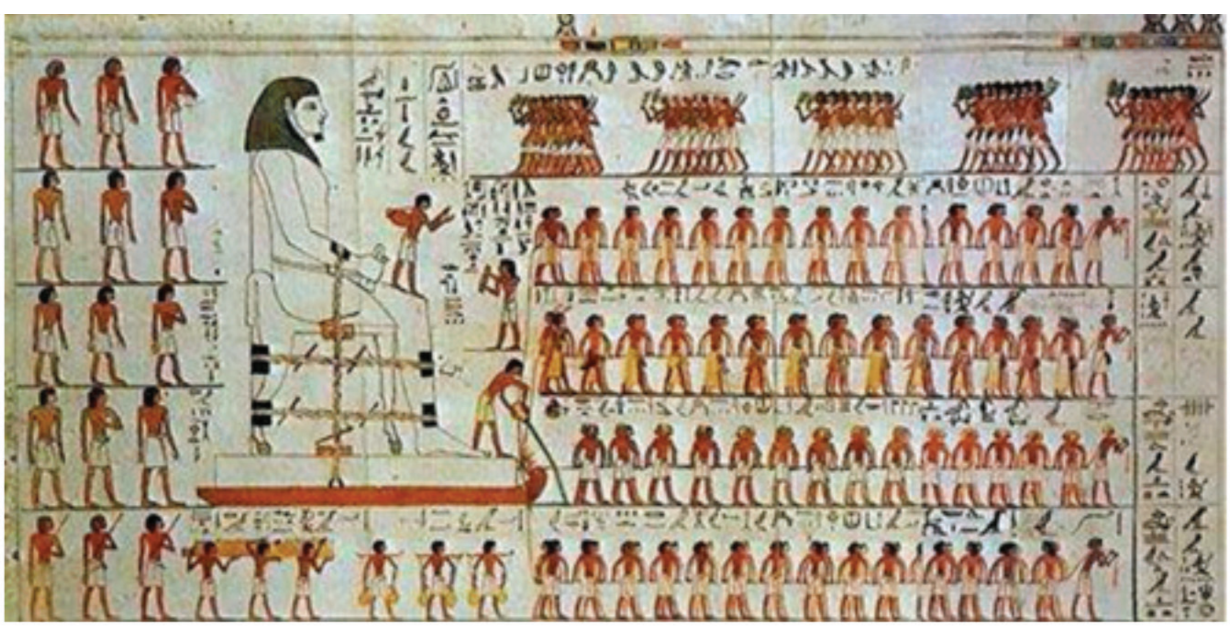

Figure 1: A wall painting from the tomb of Djehutihotep.

conducted several quantitative experiments to observe the effects of friction between different objects and surfaces [4]. He observed that different materials moved with varying degrees of ease and focused his studies on all kinds of friction systems. More specifically, he studied roughness and contact geometry between a variety of rectangular, cylindrical, and spherical systems. Although he had studied frictional systems for over 20 years, Da Vinci unfortunately never published his works or provided any mathematical theorems for his findings.

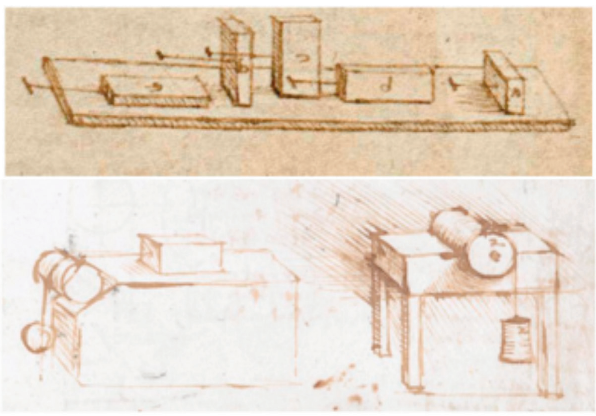

Figure 2: Sketches from Leonardo DaVinci's notebooks.

Traditionally, various organic substances, like olive oil and animal fats, were used to minimize friction forces [5]. However, the Industrial Revolution of the 18th and 19th centuries brought in new challenges: metal-based machinery needed new kinds of robust lubricants. These challenges ushered a tribological breakthrough with the use of petroleum-based lubricants. By the beginning of the 20th century, engineers and scientists realized that stand-alone oils or greases were not efficient enough for friction reduction in extreme applications and harsh conditions. Thus, beginning about a hundred years ago, lubricant additives came to play a significant role in the new wave of the industrial revolution.

Additives in oil formulations have become the primary means of improving lubricating performance properties [6]. Beginning in the 1920s, additives were incorporated to modify the oil's pour point, corrosion inhibition, anti-wear, viscosity, and extreme pressure resistance. By the 1980s one of the most popular and affordable lubricant additives for friction-reduction was soluble molybdenum disulfide, or MoS2. Friction-reduction in oils was further improved during the early 2000s with the inclusion of polymers-based additives. However, as time progressed, it became clear that such performance improvements had come to a standstill. This was until researchers began investigating the potential of nanoparticles incorporation. Nano-additives, at even very small weight percentages, reinforce the aforementioned properties, while also providing friction and wear resistance [7] and increasing flash point [8].

Tribological Discoveries in the Field of Nanoscience

After more than 25 years of basic nanoscience research and more than 15 years of focused R&D, nanotechnology applications are delivering what the scientists were hoping for: efficient, effective, and practical substance incorporation. Nano-additives may be incorporated to oils by suspending or dispersing the particles using a variety of methods, such as ultrasonication [9]. In doing so, they are able to provide the superior friction-reducing and wear-resistant properties that make nano-additives stand out from traditional additives.

Of course, the specific properties of nano-additives are highly dependent on their constituent elements, shape and size. The most common are metal oxides, which represent nearly 26% of nano-additives used in lubricants today [10]. This is followed by pure metal nanoparticles, at 23%. Metal oxides may be copper, titanium, iron, aluminum, and zinc oxides. Other types of additives include metal sulfides, such as tungsten and molybdenum disulfides, composites, nanostructured carbon and fullerene-like structures of various elements and compounds [11].

Nanoparticles have several mechanisms by which they can interact and improve the properties of a lubricant [12]. One such mechanism is through the creation of tribo-films, which are thin, protective films between the two contact surfaces. This dense, low shear film acts as the primary mechanism for reducing friction and wear. Another mechanism is the mechanical polishing or smoothening effect, which reduces the surface roughness in contact areas. This effect increases the contact area between the tribo-film layer and the metal surface, thereby reducing the coefficient of friction in operation. However, with surfaces of very high roughness, the nanoparticle additives are not able to provide sufficient polishing, and are only able to act on a self-repairing and mending mechanism. In this mechanism, the nanoparticle additives are able to fill in the microcracks on the contact surface, thereby "mending" this surface. This leads to even further friction reduction between the smoothened rubbing surfaces.

The size of the nanoparticle determines its mechanical, physical and chemical properties, and hence its tribology. The hardness of nanoparticles increases as their size is reduced, with a peak observed at different sizes depending on the nanoparticle type. Harder particles may cause damage to the surfaces and as a consequence, the optimal size of the nanoparticle must be selected for use in a lubricant [13]. The melting point of nanoparticles also drops significantly below 50 nm, depending on their chemical structure [14]; thus, the lubricant must be designed to fit the operational temperature profile of the system. Finally, the nanoparticles must disperse homogeneously in order to impart their properties to the lubricant; adding functional groups, such as surfactants or polymers, to the nanoparticles surface allows steric stabilization, limiting van der Waal interactions, and limiting aggregation in the base lubricant.

A more recent development in tribological research is the incorporation of nano-additives to water-based lubricants. A fundamental property of nanoparticles is that they are not influenced by the viscosity of the base oil, allowing for the investigation of water-based lubrication, rather than oil-based [15]. Perhaps the most important advantage of using water as a lubricant is its environmental friendliness. Most oil-based lubricants can be toxic and detrimental for the environment, and they may not be recyclable. Water, on the other hand, is a natural resource that acts as a cost-efficient alternative to oil [16]. At the same time however, water as a standalone lubricant has many inherent flaws. For instance, water has a very poor load carrying capacity due to its low viscosity, as compared to oils. Water also has very weak film thickness and may even react with the contact metals when used as a lubricant. Many of these issues can be solved with nanoparticle incorporation. With the introduction of nanoparticles, water may lead to the same energy savings, friction/wear reduction, and protective properties as many oil-based lubricants.

CASE STUDY 1: Graphene Oxide in Water

In a paper published by Dr. Liu and collaborators from the Laboratory of Tribology in Tsinghua University, China, the authors investigated the properties of graphene oxide (GO) nanosheets and modified diamond (MD) nanoparticles as additives to water-based lubricants [15]. The experiment aimed to study the effects of friction and subsequent wear scars of a Si_3N_4 ball sliding against an Al_2O_3 plate in a micro-tribotester, using a white light interferometric surface profiler. Graphene nanoparticles have long been researched for potential application as a lubricant additive. In a study by Z. Li et al, the concentration of graphene with the best anti-friction and anti-wear properties in a graphene/cyanobiphyl liquid crystal suspension was only 0.15 wt.%. Graphene, however, has very poor dispersibility in water and this limits its direct use with water [17]. The researchers therefore synthesized hydrophilic graphene oxide nanosheets that had improved water dispersibility characteristics. Furthermore, since nano-additive performance is highly dependent on particle size and morphology, the researchers used modified diamond (MD) nanoparticles of similar size to establish a fair experimental comparison.

To characterize the GO nanosheets and MD nanoparticles, the authors primarily used ultraviolet-visible (UV-vis) spectroscopy. They dropped 2 µL of the GO colloid at 0.0002% mass concentration onto a mica surface. The same procedure was followed for the MD colloid, but at a 0.0005% mass concentration. The GO and MD droplets topography was then analyzed under an atomic force microscope (AFM) using the tapping mode.

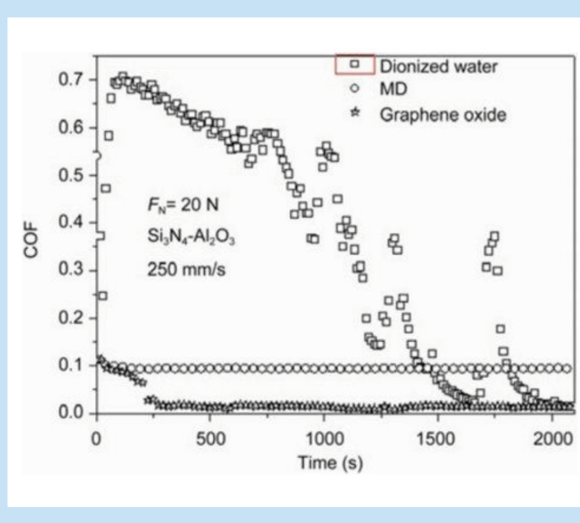

Figure 3. Coefficient of friction (CoF) over time.

In order to measure the coefficient of friction (CoF) during the experiment, the authors employed a universal micro-tribotester. This instrument measured the CoF every 0.4 seconds as the Si_3N_4 ball came into contact with the moving Al_2O_3 plate. The authors then were able to generate a plot of the CoF of these particles over time, shown in Figure 3. As it can be observed, both the MD and GO particles significantly reduced the test system's friction. Graphene oxide had a higher initial coefficient of friction, or CoF, but it went drastically down after about 250 seconds. The MD particles, on the other hand, demonstrated constant CoF throughout the experiment. These results were compared to a deionized water control group, which had a varied but negative correlation of CoF over time.

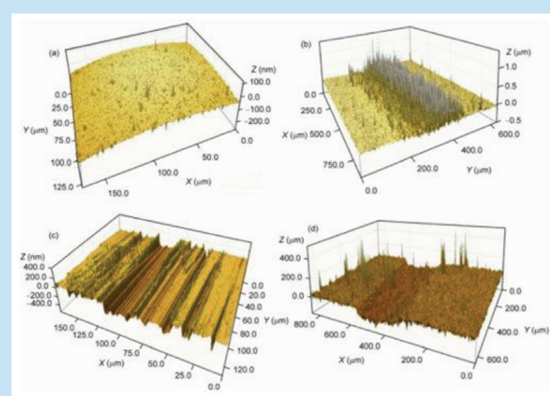

Figure 4. 3-D profiles of wear scar on the Si_3N_4 ball (a) and the Al_2O_3 plate (b) after friction experiment lubricated by GO colloid; 3-D profiles of wear scar on the Si_3N_4 ball (c) and the Al_2O_3 plate (d) after friction experiment lubricated by MD colloid.

Furthermore, as shown in Figure 4, a white light interferometric surface profiler was used to generate three-dimensional morphology profiles of the Si_3N_4 ball and the Al_2O_3 plate. The first two images on the top show the effects of using the GO colloid on the ball and plate, whereas the bottom two images show the impact on the ball and plate when using the MD colloid. With the GO colloid, the ball surface remained extremely smooth, especially compared to that of MD use. Spikes are present in the image of the plate surface after the use of GO. These spikes represent the agglomeration of nanoparticles on the surfaces. When comparing the GO and MD particles, it is clear that GO provides far superior wear resistance. The use of MD particles created significant wear on both the Si_3N_4 ball and Al_2O_3 plate as it can be seen from the varying thickness and the conspicuous roughness throughout the surface, respectively.

Comparing Additives

As discussed earlier, there are many different types of nano-additives, with each constituent element providing unique advantages to a final product. Some of the most well-performing nano-additives are molybdenum and tungsten disulfides, especially in the shape of inorganic fullerene-like structures [11]. These disulfides are commonly used in greases. A significant challenge in using these sulfides as lubricants is their high insolubility in liquids, which can be overcome with appropriate means of surface functionalization.

Alternatively, pure metal nanoparticles are used in lubricant solutions. Pure metal nanoparticles are able to drastically reduce the friction and wear between contact surfaces by the formation of a tribo-layer. In addition, they have been found to exhibit excellent self-healing and mending properties. These metals may include Fe, Cu, Co, and Ni. As an example, in a study of Ni nanoparticles, researchers have found that the Ni particles are able to deposit onto the friction surfaces, protecting such surfaces from wear [11].

Metal oxides, such as TiO_2, are of the most commonly used additives in lubricants. They are known to exhibit some of the best anti-friction and anti-wear properties. Common types of metal oxides include Fe, Cu, and Al as the metal component. Some of the best metal oxide lubricants are composite blends (hybrid nanomaterials), such as Al_2O_3 with TiO_2 or ZrO_2 with SiO_2.

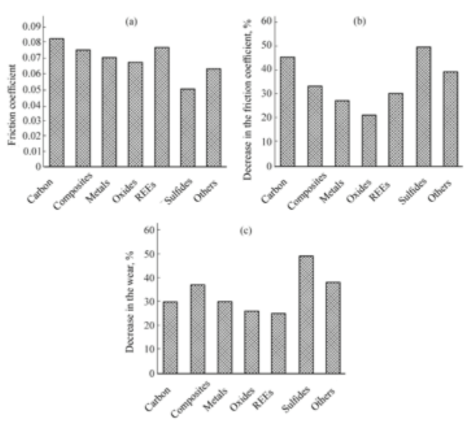

Figure 7. Comparing tribological properties by constituent elements.

Figure 7 above compares various friction and wear properties of different particles. As it can be seen in all three categories, metal sulfides provide superior performance. Not only do they have the least coefficient of friction, but they are also able to reduce the most amount of wear on contact surfaces under operational conditions. It can also be noted that oxide and REE (rare earth element) nanoparticles are underperformers in all three categories.

Conclusion

The capacity of nanoparticles, namely graphene oxide and TiO_2, for improving the tribological properties of water-based lubricants was shown to be excellent in the two case studies discussed. However, not all of the nanoparticle-based water dispersions possess the same qualities. Although graphene oxide and titanium oxide are well known solid additives, they exhibit minor enhancements to the base fluid with moderate friction reduction properties when used at high concentrations. As of now, the most potential can be found with fullerene-like molybdenum and tungsten disulfides. Nearly spherical, submicron particles of tungsten disulfide enhance the tribological performance far better than their commercial macroscale counterparts. The main challenge for implementing these disulfides in lubricants is their high liquid insolubility. Furthermore, sulfur content as a whole is highly regulated by a variety of environmental groups. A better alternative could be to use these sulfides as water-based lubricants, allowing them to be less toxic towards the environment.

Although there are a few commercial nano-additives in use today, they are still not as established as the more widely used oil-based lubricants. However, as oil standards set by agencies, such as the ILSAC or API, become more rigorous, nano-additives will play a significant role in improving oil performance and efficiency. Until then, there needs to be much more research and testing to investigate the potential of nanoparticle additives in the laboratory and also in large-scale.

CASE STUDY 2: Titanium Oxide in Water

In another investigation into the use of water-based lubricants, Dr. Hui Wu and researchers from the University of Wollongong (China), University of Queensland (Australia), and Baosteel Research Institute (China) studied the tribological behavior of titanium oxide (TiO_2) nanoparticles in water [18]. Here, the researchers once again analyzed tribological behaviors and the effects of nanoparticles on the friction coefficient. The authors were also able to discuss the various lubrication mechanisms that are responsible for such friction-reducing properties. A ball-on-disk tribometer was used in this study. This instrument allows for efficient bench testing for lubricants by measuring wear volume between a ball and disk system in contact.

In order to prepare the lubricant, the titanium oxide particles were mechanically stirred and mixed with deionized water. The researchers then added to the mixture polyethylenimine (PEI), which is a polymer that improves dispersion of nanoparticles in water. After centrifugation, glycerol was added to increase viscosity. Lastly, the mixture was ultrasonicated to break down any agglomerates in the solution.

The researchers employed a variety of techniques to obtain characterization data. They first used powder X-ray diffraction to characterize the actual titanium oxide nanoparticles. To generate micrographs and determine size distribution, transmission electron microscopy and energy-dispersive spectrometry was used. Furthermore, UV-vis spectrophotometry was employed to determine suspension stability. And finally, laser scanning and scanning electron microscopes were used to observe and generate wear profiles on the balls and disk systems.

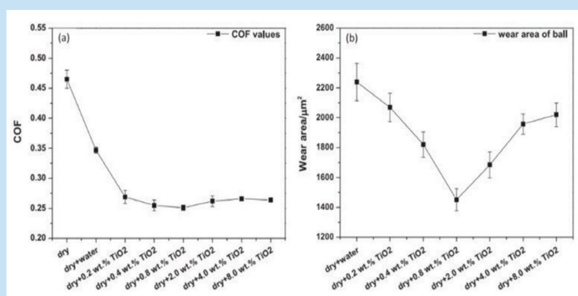

Figure 5. Coefficient of friction and wear areas of the balls (5 min dry and 5 mins lubricated).

In this study, the researchers measured the CoF after allowing the ball to rotate dry for 5 minutes, and lubricated for another 5 minutes. The lubricant solutions were tested at varying weight percentages of TiO_2. The results, as shown in Figure 5, confirmed their hypothesis that the use of TiO_2 significantly improves the anti-friction properties of the water-based lubricant. The best performance results, with both the lowest CoF and wear area, was reached at a TiO_2 weight percentage of 0.8. An increase in the treat rate significantly increased wear. It is assumed that at weight percentages greater than 0.8, the increased wear area is a result of the poor dispersion of the nanoparticles and the formation of agglomerates in the system.

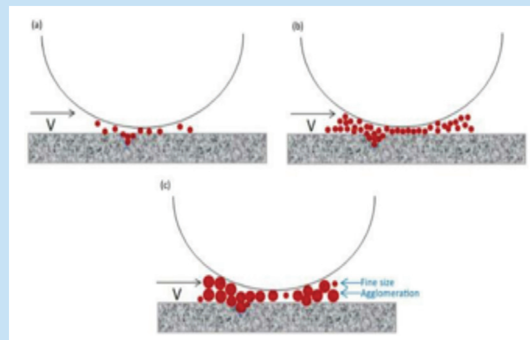

Figure 6. Lubricating mechanisms of TiO_2 at 0.2 %, 0.8 %, and 4.0 % (by weight).

After the experiment, the authors then wanted to investigate the mechanisms of TiO_2 lubrication, as well as the formation of agglomerates when increasing TiO_2 weight percentage. Using the scanning electron microscope and energy dispersive spectrometer, they were able to generate a schematic of these mechanisms, as shown in Figure 6. At a low 0.2 weight percentage, the system does not have enough lubrication to reduce friction efficiently, thus leading to a significant wear area. At 0.8 weight percentage, however, the system has optimal lubrication and can fill the microcracks on the surface, while also creating somewhat of a tribo-film between the two surfaces. When increasing to a much higher weight percentage of 4, there is a significant agglomeration, negatively impacting the formation of uniform and smooth tribo-film and thus, the overall friction coefficient.

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