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 of 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...
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 THE SIZE 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.

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 PRINCIPAL SUBSTANCE INCORPORATION. NANO-ADDITIVES MAY BE INCORPORATED TO OILS BY SUSPENDING OR DISPENSING 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.


A MORE RECENT DEVELOPMENT IN TRIBOLOGICAL RESEARCH IS THE INCORPORATION OF NANO-ADDITIVES TO WATER-BASED LUBRICANTS. A FUNDAMENTAL PROPERTY OF NANO-PARTICLES 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 RECIRCULABLE. 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 NANO-PARTICLE INCORPORATION. WITH THE INTRODUCTION OF NANO-PARTICLES, 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 AT Tsinghua University, China, THE AUTHORS INVESTIGATED THE PROPERTIES OF GRAPHENE OXIDE (GO) NANOPARTICLES 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 ON A Si3N4 BALL SLIDING AGAINST AN Al2O3 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 WEAR-REDUCTION EFFECTS IN A GRAPHENE-CYANOPHENYL LIQUID CRYSTAL SUSPENSION WERE 0.02% BY VOLUME. GRAPHENE, HOWEVER, HAS VERY POOR DISPERSIBILITY IN WATER AND THIS LIMITS ITS DIRECT USE WITH WATER [17]. THE RESEARCHERS THEREFORE SYNTHESIZED HYDROGENIC GRAPHENE OXIDE AND ANTI-FRICTION-ACTING ADDITIVES IN A GRAPHENE CYANOPHENYL LIQUID CRYSTAL SUSPENSION.

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 Si3N4 BALL CAME INTO CONTACT WITH THE MOVING Al2O3 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 A 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.
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 functionality.

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 TiO₂, 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 Fe₂O₃, CuO, and Al₂O₃ as the metal component. Some of the best metal oxide lubricants are composite blends (hybrid nanomaterials), such as Al₂O₃ with TiO₂ or ZrO₂ with SiO₂.

Conclusions

The capacity of nanoparticles, namely graphene oxide and TiO₂, 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 challenge in using these sulfides as lubricants is their high liquid insolubility. Metals like copper, iron, cobalt, and nickel are underperformers in all three categories.

Figure 7 above compares various friction and wear properties of different nanoparticles. 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.

References

About the Authors

Dr. Raj Shah is a Director at Koehler Instrument Company in New York, where he has worked for the last 25 years. He is an elected Fellow by his peers at IChemE, CMI, STLE, AIC, NLGI, INSTMC, The Energy Institute and The Royal Society of Chemistry An ASTME Eagle award recipient, Dr. Shah recently coedited the bestseller, “Fuels and Lubricants handbook”, details of which are available at https://www.astm.org/DIGITAL_LIBRARY/MNL/SOURCE_PAGES/MNL37-2ND_foreword.pdf

A Ph.D in Chemical Engineering from The Penn State University and a Fellow from The Chartered Management Institute, London, Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering council, UK. An adjunct professor at the Dept. of Material Science and Chemical Engineering at State University of New York, Stony Brook, Raj has over 300 publications and has been active in the petroleum field for 3 decades. More information on Raj can be found at https://www.petro-online.com/news/fuel-for-thought/13/koehler-instrument-company/dr-raj-shah-director-at-koehler-instrument-company-conferred-with-multifarious-accolades/53404

Dr. Steve (Stephanos) Nitodas is currently a member of the Faculty of the Department of Materials Science and Chemical Engineering at Stony Brook University, NY. His expertise lies in the synthesis and applications of nanostructured carbon and polymer nanocomposites. He has served as Coordinator/Principal Investigator in five (5) EU funded research projects of 4.2 million Euro total budget, and he has been involved as Co-Principal Scientist in thirteen (13) other funded research projects. Dr. Nitodas has worked for several years in the nanotechnology industry, possessing significant know-how related to transfer of knowledge from academia to the industry and the setup of startup companies.

Mr. Sarjeel Zaman is part of a thriving internship program at Koehler Instrument company and a student of chemical engineering at State University of New York, Stony Brook, where Dr. Shah currently heads the External advisory board of directors.

Author Contact Details

Dr. Raj Shah, Koehler Instrument Company  •  Holtsvile, NY 11742 USA  •  Email: rshah@koehlerinstrument.com  •  Web: www.koehlerinstrument.com

David Phillips, Content Editor, Petro Industry News, david@pin-pub.com