Dr. Neil Canter / Contributing Editor

EP nanoparticles-based lubricant package

These multifunctional, eco-friendly lubricants use a patent-pending process that exhibits lubricity and EP characteristics.

Update: In the March Tech Beat article titled, "BAM: Antiwear and friction-reducing coating," the research on the alloy of boron-aluminum-magnesium nicknamed BAM was conducted by the U.S. Department of Energy's Ames Laboratory. Alan Russell is an Ames lab scientist and professor of material science and engineering at Iowa State University. Bruck Cook is an Ames lab metallurgist. The figure was provided courtesy of the U.S. Department of Energy's Ames Laboratory.

KEY CONCEPTS:

- A new organic-inorganic nanoparticle-based package provides superior antiwear, friction-reducing and extreme pressure properties.
- The organic-inorganic nanoparticle-based package exhibits a lower wear scar diameter, coefficient of friction and a higher weld point than a dispersion of molybdenum disulfide in paraffinic oil.
- The properties of the organic-inorganic nanoparticle-based package can be tailored to meet specific applications.

Lubricants are needed to minimize the amount of friction and wear generated in machinery. In carrying out this function, lubricants need to be situated on the surfaces of metals and other substrates.

With many of the interactions between lubricants and metal surfaces occurring at the molecular level, there is a greater need to better understand how such basic lubricant additives as antiwear and extreme pressure (EP) agents perform at the nanoscale.

In previous TLT articles, discussions have been held about the growing field of nanotribology.[1] Commercial products containing nanoparticle-based additives are growing in use to meet a variety of applications. Development of nanoparticle-containing lubricants and lubricant additives has been slow with problems encountered in stabilizing these species in carriers such as mineral oil.

Dr. Ajay Malshe, chief technology officer for NanoMech™, LLC, in Fayetteville, Ark., says, "Current nanoparticles for use as antiwear and EP agents are based mainly on inorganic chemistries that are applied as solid coatings or used in mineral oil-based dispersions. Solid coatings will perform well for a time but tend to be worn away due to the presence of sharp asperities. Inorganic-based nanoparticle oil dispersions are not stable, and the lubricant additive readily precipitates out or agglomerates into larger particles that are ineffective."

Organic-based additives have not been found to be an option because they do not provide adequate antiwear and/or EP performance. One other factor in working with current additives of these types is that they have been under regulatory scrutiny for at least 25 years.

STLE-member Dr. Arpana Verma, senior product engineer at NanoMech, LLC, says, "In addition to performance, the drive is toward multifunctional, environmentally friendly lubricants whose cost is comparable to current products."

Development of nanoparticles that can exhibit antiwear and EP performance, be compatible with current lubricant basestocks and exhibit even more environmentally friendly characteristics would be welcomed in the marketplace. Such a technology has not been available until now.

ORGANIC-INORGANIC NANOPARTICLE-BASED PACKAGE

NanoMech has integrated layered inorganic solid lubricant nanoparticles of molybdenum disulfide with canola oil to form a solid lubricant package using a patent-pending process that exhibits lubricity and EP characteristics. The product has been commercialized and is known as NanoGlide.®

Verma says, "We used a chemo-mechanical process to integrate molybdenum

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disulfide with the canola oil. This is an example of the flexibility of this manufacturing process. The unique process has allowed multiple chemical combinations that can address varying application demands." Figure 1 shows the proposed design of a package based on a molybdenum disulfide nanoparticle that contains canola oil and lecithin.

The same synthesis technique has been applied to other application-specific components such as ZDDP, MoDTP, borates and others to design and develop improved compatible lubricants. This also was explored with other solid lubricants, including tungsten disulfide and graphite. As a result, the EP nanoparticles-based package can be easily inserted into current lubricant systems.

The organic-inorganic nanoparticle-based package also can be readily incorporated into most conventional basestocks used in the preparation of lubricants. These include base oils (Group I and Group II), synthetics (such as polyalphaolefins and esters) and biodegradable feedstocks. The nanoparticle-based package also can be formulated into greases.

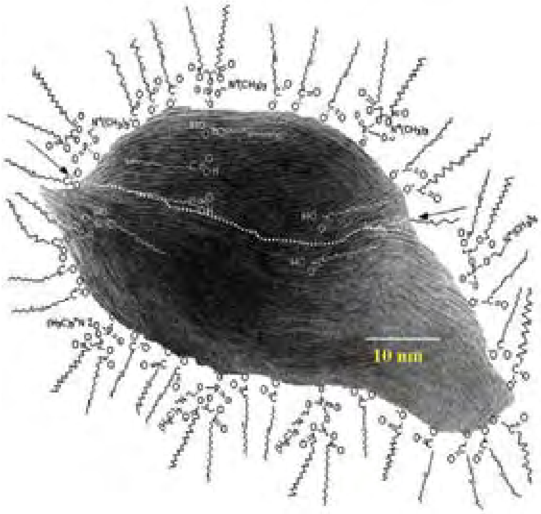

Figure 1 | **The proposed image of an organic-inorganic nanoparticle-based package shows a molybdenum disulfide nanoparticle surrounded by canola oil and lecithin (phospholipid) molecules.** *(Courtesy of NanoMech™ LLC)*

Four-ball wear (ASTM D4172) and the four-ball extreme pressure (ASTM D2783) methods were conducted on the organic-inorganic nanoparticle-based package at a 1% dispersion in paraffinic oil. Wear testing was run at 75 C with the AISI 52100 steel balls being rotated at 1,200 rpm for 60 minutes at a load of 40 kg. The wear scar diameter and the coefficient of friction for the organic-inorganic nanoparticle-based package derived from molybdenum disulfide and canola oil are 0.46 millimeters and 0.07, respectively.

In contrast, paraffinic oil with a 1.0% dispersion of molybdenum disulfide nanoparticles prepared just by simple processing displays a much higher wear scar diameter of 0.95 millimeters and a higher coefficient of friction of 0.09.

In EP performance testing under standard conditions, 1.5% of the organic-inorganic nanoparticle-based package displayed a weld point of 315 kg. In contrast, 1.5% of molybdenum disulfide, which was produced by a simple process, showed a weld load of less than 150 kg.

Verma says, "The test results show that the organic-inorganic nanoparticle-based package exhibits better stability in lubricant oil basestock, which translates into superior antiwear, friction-reducing and extreme pressure properties." The use of canola oil also means that the organic-inorganic nanoparticle-based additive is environmentally friendly and can provide good sustainability.

Other types of lubricant additives can be incorporated into the organic-inorganic nanoparticle framework, as well. Verma adds, "We have also included sulfur- and phosphorus-based technologies in the matrix to tailor the properties of the organic-inorganic nanoparticle-based package to meet specific applications. The flexibility of the organic-inorganic nanoparticle should be of value in meeting the increasing demands placed on lubricants to function under more severe conditions over longer operating intervals."

Malshe and Verma believe that the organic-inorganic nanoparticle-based package can be utilized in automotive lubricants, biodegradable lubricants, gear oils for multiple industries (earth movers and heavy machinery for infrastructure development, naval ships, etc.), greases and metalworking fluids. In the latter application, the organic-inorganic nanoparticle-based package was found to increase the G-ratio and reduce friction in minimum quantity lubrication grinding of cast iron.[2]

Additional information can be found in a recent article in STLE's peer-reviewed journal, *Tribology Transactions*.[3] Further details about the organic-inorganic nanoparticle-based additive can be obtained by contacting Verma at **arpana.verma@nanomech.biz.**

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New technique: Analyzing nanoparticles in lubricants

Originally developed to evaluate viruses in water-based systems, Nanoparticle Tracking Analysis measures and quantifies nanoparticles in oil.

Varnish buildup remains a constant threat to optimum lubricant performance over a long period of time. This material is formed through the polymerization and agglomeration of insoluble, oil degradation byproducts. These species are generated due to thermal, mechanical and electrostatic spark discharge stresses placed on the lubricant.

Varnish is amorphous and can be found in a range of colors and consistencies. It also consists of particles that are less than 1 micron in diameter. This makes analysis of varnish very difficult and problematic. In a previous TLT article, a colorimetric technique called Quantitative Spectrophotometric Analysis (QSA) was described.[1] This method predicts the level of varnish in a lubricant system to an accuracy of +/- 10%.[1]

STLE-member Gerald Munson, CLS, managing partner of Fluid Assets, LLC, in Madison, Conn., says, "There is need for a better technique to quantify the number of and size of nanoparticles in an industrial lubricant such as turbine oil. Analytical procedures such as PCS (Photon Correlation Spectroscopy of DLS, Dynamic Light Scattering) have been available to detect and evaluate nanoparticles, but they have limitations."

PCS provides useful data on nanoparticles, but it has a significant weakness when particles of different sizes are present. Munson explains, "Large particles interfere with the ability of PCS to measure the size and amount of smaller nanoparticles." In the real world of lubrication systems, as we all know, particles come in many different shapes and sizes.

NTA measures the size and quantity of submicron particles through the use of video microscopy by tracking the Brownian Motion of particles in all types of liquids.

Development of a technique that can more accurately measure smaller nanoparticles that are frequently contributors to lubricant and machinery failure is needed. Such a technique has not been available until now.

NANOPARTICLE TRACKING ANALYSIS

A technique just developed over the past few years by Fluid Assets measures and quantifies nanoparticles of many different sizes in oil. It is known as Nanoparticle

KEY CONCEPTS:

- Nanoparticle Tracking Analysis has been developed to determine the type and quantity of nanoparticles in lubricant oil.
- Brownian Motion of the nanoparticles makes their analysis more challenging. Parameters such as viscosity, refractive index and temperature must be known to obtain accurate NTA.
- The accuracy of the NTA test, considered to be an important supplement to the QSA test, is better than +/- 5%.

> ‘Water is very transparent, and a high contrast can be seen between clean and relatively contaminated water. The viscosity of water is also low, which helps with the analysis.’

Tracking Analysis (NTA) Model OM-30.

Munson indicates that NTA was developed for use in biological applications in water-based systems. He says, “The initial application of NTA is to evaluate viruses, which typically range in size from 10 to 100 nanometers.”

NTA measures the size and quantity of submicron particles through the use of video microscopy by tracking the Brownian Motion of particles in all types of liquids. The imaging is done by focusing a fine laser beam of light with a wavelength of 638 nanometers through a sample containing the nanoparticles. These particles are seen by an optical microscope and then analyzed with proprietary software.

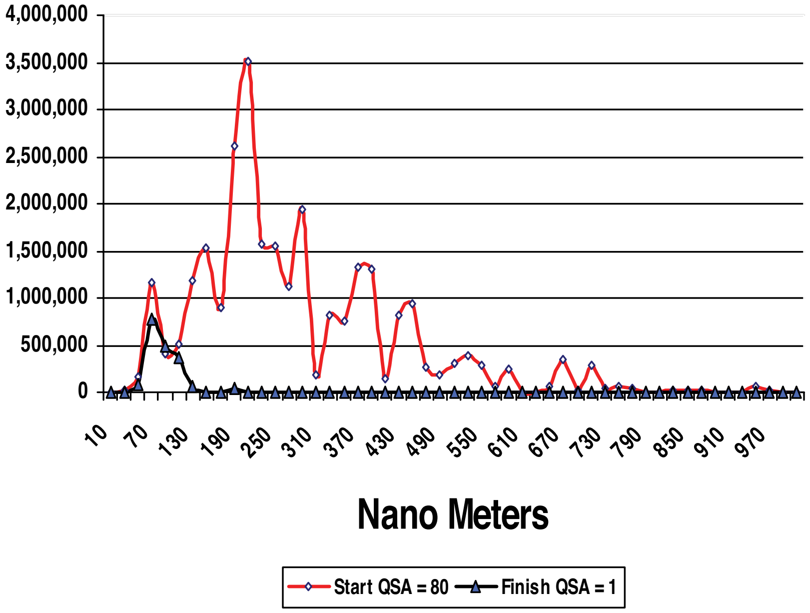

Figure 2 | **Nanoparticle Tracking Analysis (NTA) determines the type and quantity of nanoparticles in a specific turbine oil system, as shown in the curves. The red curve shows the nanoparticles prior to system cleanup, while the blue curve displays the nanoparticles left after filtration.** *(Courtesy of Fluid Assets, LLC)*

Water has proven to be a fairly easy medium to use in NTA analysis. Munson says, “Water is very transparent, and a high contrast can be seen between clean and relatively contaminated water. The viscosity of water is also low, which helps with the analysis.”

In contrast, using NTA to do particle analysis in oils is much more challenging. Munson adds, “Viscosity and refractive index vary depending upon the oil. Temperature is also a critical factor to ensure that the results are accurate. The reason is that these parameters all affect the Brownian Motion of the nanoparticles. We have developed a technique to overcome these difficulties.”

On the higher particle size end, NTA is able to detect and quickly evaluate particles up to a size of 0.8 microns. Munson adds, “At particle sizes above 1-2 microns, the time required to track particles is too long to be practical.” This capability dovetails nicely with existing and new ASTM standards such as the F-312 patch test down to 0.5 micron and those being developed.

The accuracy of the NTA test is better than +/- 5%, according to Munson. From a precisions standpoint, additional testing is needed to evaluate a larger number of samples.

The ability of NTA to determine the type and quantity of nanoparticles in a specific turbine oil system is shown in Figure 2. The red curve shows the number of nanoparticles by quantity (count on the y axis) and size (on the x axis) for the system prior to being cleaned up. Afterward, the blue curve displays the reduction in the number of nanoparticles in the lubricant system over a broad range of particle sizes in one pass through a unique electronic kidney loop filtration system.

Munson sees NTA as an important supplement for the QSA test. He adds, “We hope that the data generated by NTA will prove to be as important as results obtained from existing varnish tests.”

Munson is continuing to collect NTA data from mainly turbine oil systems to better understand the capabilities of the method. Future work will involve evaluation of lubricants formulated with other synthetic basestocks such as esters and polyalkylene glycols.

Further information can be obtained by contacting Munson at **gmunson@fluid-assets.com**. He will also be presenting a paper on NTA at the upcoming 2009 STLE Annual Meeting & Exhibition in May.

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Biodegradation of carbon nanotubes

Researchers have discovered a naturally occurring enzyme as a potential candidate that can degrade these unique nanomaterials.

KEY CONCEPTS:

- A naturally occurring enzyme known as horseradish peroxidase has been found to biodegrade carbon nanotubes.
- Used with hydrogen peroxide, HRP degrades carbon nanotubes over a 16-week period at 4 C. The process accelerates at elevated temperatures.
- The active component doing the decomposition is an iron (IV) porphyrin radical cation formed from the oxidation of HRP by hydrogen peroxide.

The strong interest in nanotechnology and the development of new nanomaterials has led to some concern about their potential toxicity. Nanomaterials are typically between 1 and 100 nanometers in size. As a comparison, the diameter of one human hair is 10,000 times larger than 1 nanometer.

As more and more commercial products have been developed with nanomaterials, concern has arisen about their safe use, particularly when placed in contact with human beings. For example, titanium dioxide is used widely as a pigment in cosmetic products such as sunscreens. Conventional titanium dioxide is white in appearance while nano-sized titanium dioxide is transparent. Does conventional titanium dioxide used in the past have a comparable health and safety profile to titanium dioxide nanoparticles?

One notable nanomaterial is carbon nanotubes, which is composed of thick rolls of graphite that are also stronger than steel. In a previous TLT article, the precursor to carbon nanotubes, graphene, was found to be the strongest material ever examined.[1]

> 'The toxicity of carbon nanotubes is controversial. There are some reports that carbon nanotubes, if inhaled, can cause respiratory inflammation in a similar manner to asbestos.'

Carbon nanotubes have found use in a variety of applications, including reinforcing plastics, conducting electricity in electronics and as sensitive chemical sensors. Alexander Star, assistant professor in the department of chemistry in the University of Pittsburgh's School of Arts and Sciences, says, "The toxicity of carbon nanotubes is controversial. There are some reports that carbon nanotubes, if inhaled, can cause respiratory inflammation in a similar manner to asbestos." Other potential negative effects include formation of free radicals and peroxidative products.

But identification of a potential safety problem is more complicated because carbon nanotubes have been produced in many different forms. Star adds, "Carbon nanotubes have been found with different lengths and have been prepared in large bundles or ropes. Functionalization has also produced different nanotubes with new characteristics."

With the growing use of carbon nanotubes, there is an increasing chance of environmental pollution and exposure. Development of a safe method for decomposing carbon nanotubes is desired. Such a technique has not been available until now.

Safe decomposition of carbon nanotubes is quite challenging because of the nature of the material.

NATURAL HORSERADISH PEROXIDASE

Safe decomposition of carbon nanotubes is quite challenging because of the nature of the material. Star says, “The carbon-carbon bonds in carbon nanotubes are the strongest found in nature and are extremely robust.”

The researchers identified the natural enzyme horseradish peroxidase (HRP) as a potential candidate to degrade carbon nanotubes. Star says, “HRP became a plausible option because it is known to biodegrade different organic compounds, including polyaromatic hydrocarbons that are close in composition to carbon nanotubes. This enzyme is also very robust and works well over a broad range of temperatures.”

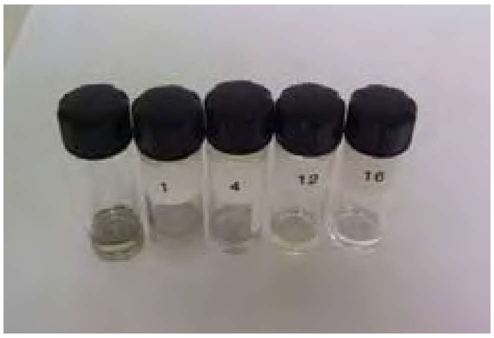

Figure 3 | **The enzyme horseradish peroxidase (HRP) slowly degrades carbon nanotubes at 4 C over a 16-week period. Samples taken at weeks 1, 4, 12 and 16 become more transparent as the study progresses, which indicate the carbon nanotubes are being degraded.** *(Courtesy of the University of Pittsburgh)*

The carbon nanotubes evaluated by the researchers were initially oxidized with a combination of sulfuric acid and hydrogen peroxide to remove residual metal catalyst. This step also carboxylated the carbon nanotubes to enable them to be soluble in an aqueous environment.

HRP was then added to the carboxylated carbon nanotubes in the presence of hydrogen peroxide and the mixture incubated for 16 weeks at 4 C at a pH of 7. Star says, “We used a low concentration of hydrogen peroxide because of its compatibility with HRP. The mixture was kept in the dark to avoid enzyme degradation and the photolysis of hydrogen peroxide.”

A number of different analytical techniques were conducted to evaluate the condition of HRP and determine the concentration of carbon nanotubes present in the mixture during the study. Electron spin-resonance analysis showed that the HRP remained viable and was not deactivated by the carbon nanotubes.

Over the 16-week period, aliquots of the mixture were removed for evaluation and were replaced by an equal volume of hydrogen peroxide. Star says, “Using the naked eye, we could see the concentration of nanotubes decrease from the beginning of the study through week 16. The initial gray color declined in intensity during that time and the mixture displayed more and more transmittance.”

Figure 3 shows samples taken at the beginning of the study and after weeks 1,4,12 and 16. Clearly the mixture is becoming more transparent over the duration of the experiment. Light scattering measurements verified the increase in transmittance. Degradation of the carbon nanotubes was confirmed by transmission electron spectroscopy, which showed a decrease in the length of the carbon nanotubes and the concomitant appearance of globular material.

The process can be accelerated by using higher temperature and larger concentrations of hydrogen peroxide. Star says, “Carboxylated carbon nanotubes were incubated with HRP at 37 C for five days with hourly additions of hydrogen peroxide. Over that time frame, 40% of the carbon nanotubes were decomposed. We believe this moves the decomposition of carbon nanotubes from weeks to days, but there is still room for optimization.”

The degradation has been attributed to the formation of a highly reactive intermediate. Star explains, “The active site of the HRP is an iron (III) porphyrin ring complex. Oxidation with hydrogen peroxide generates an iron (IV) porphyrin radical cation that decomposes carbon nanotubes by reducing their length.”

Work is in progress to better understand what species are formed during degradation of the carbon nanotubes. Star says, “We are using mass spectroscopy to identify the molecules present and will use HPLC to isolate the individual components.”

Future work will involve using HRP on other carbon nanotubes that have different lengths and different structures such as number of walls. Details about the research can be found in a recent article.[2]

The work described here is an important step in dealing with potential concerns that will arise from the increasing presence of nanomaterials in consumer and industrial products. TLT

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