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Final Report

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Energy Efficiency, Durability
and Lower Maintenance Costs
of Advanced Naval Components
and Systems**

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Abstract

In boundary lubrication, spacing of mating surfaces in direct physical contact is in the scale of surface asperities. These conditions may benefit from the nanoscale dimension of the advanced nanoparticle lubricants in the following ways: (1) by supplying nano to sub-micron size lubricating agents which reduce friction and wear at the asperity contact zone, (2) by enabling strong metal adsorption and easy wetting, (3) by reacting with the surface to form durable lubricating “transient transfer” films, sustain high loads and also remain under high temperatures, and (4) by enabling all these at minimal cost and great environmental safety. These materials specifically designed on antiwear and extreme pressure chemistries can significantly lower the sulfur and phosphorus level in the lubricant additive and therefore provide environmental benefits.

The project encompasses a detailed investigation of advanced nanolubricants that favorably impact robust boundary film formation to reduce wear and friction. These active nanolubricant additives are designed as surface-stabilized nanomaterials that are dispersed in a hydrocarbon medium for maximum effectiveness. This effort is focused on developing active nanoparticle composites, optimizing process design, physical and chemical characterization of nanomaterials, detailed tribological film characterization, and tribological testing to document friction and wear improvements.

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Summary

In this project we are developing extreme-pressure additives based on surface modified nanoparticles of molybdenum sulfide (MoS_2). These additives are based on “green” surface chemistries and will have application in the many heavy duty lubrication systems used by the Navy, imparting lower friction, higher reliability, and longer life, leading to reduced energy usage and increased mission availability. They will also have potential for use throughout commercial industries.

In the third quarter of this project, two initial formulations of the nanolubricant were modified to specifically address their application as additives in gear oils and greases. These improved formulations were investigated through chemical, structural, and tribological analysis. A Design of Experiments (DoE) approach for synthesis and optimization using scaled up production equipment was applied to analyze interaction between process parameters and to select optimal synthesis parameters to be used with optimal process time.

Tribological testing of nanolubricant additives in gear oils using Pin-on-Disk test and Block-on-Ring test, and in greases using 4 Ball test and EP 4 Ball test was performed. An evaluation and comparison of their performance is presented and discussed in this report. Equipment that will be used for FZG testing is being prepared to support FZG tests that will test the nanolubricant formulations with actual gears using a standard test protocol.

For the WAM High Speed Test, Air BPTO 25 with specification DOD-PRF-85734 aircraft gearbox oil was chosen as the reference oil. This oil formulation gave a scuffing failure stage of 19.5 with no micro-scuffing event. To this oil, nanolubricant formulation was added for pre-screening. However, due to competing anti-wear and extreme pressure chemistries in the BTPO 25 oil and nanolubricant additive, a lower scuffing failure stage of 17.0 was observed. This realization led to the synthesis of a new nanolubricant formulation L1NG1D2WX in BPTO 25 oil and a higher scuffing failure stage of 23.0 was observed with one micro-scuffing event. While this micro-scuffing action actually restores some of the EHD fluid film separation between the surfaces, the rapid removal of surface features by plastic flow and rapid polishing wear reflects a failure of the oil formulation to provide adequate surface films for boundary lubrication. Thus, the nanolubricant additive was re-

formulated and 2% 2KDS16-1 in BPTO 25 oil demonstrated a higher scuffing failure load stage of 24.5 with no micro-scuffing event indicating the high load-carrying capacity of the additive package.

This project has revealed several advantages of having nanolubricant in lubricant formulations (gear oils and greases). It provides advanced lubrication for severe friction conditions (extreme pressure and loads) by extending component life and lube-drain intervals in comparison with base oils and greases. It is a technology that could increase the efficiency and durability of machinery components particularly gears, leading to longer operation intervals and lower maintenance costs. Another beneficial feature is that it is non-disruptive and insertable into current lubricant production processes, and there is a wide range of industrial applications in which it can be put to use with similar advantages.

The scaled-up production process was developed and process parameters were optimized. Morphological and tribological properties of samples from larger-scale production were compared with properties of samples from laboratory-scale production. This comparison demonstrated the ability to achieve a similar particle size distribution without any significant increase in the level of agglomeration of nanoparticles, and a shortened process time for the scaled-up production process. This contributes to the technical objective of extended shelf life and suspension stability of the nanoparticle additives, and to the commercial goal of increasing yield per batch with significant reduction of the processing time.

Introduction

This project focuses on research and development of active family of nanolubricant additives, for applications in the US Navy. In previous work, NanoMech has explored the fundamental science of nanoparticle design and synthesis using a top-down synthesis process, including the mechanisms of synthesis, interaction of “simple organic and inorganic materials” for de-agglomerated nanostructures, dispersion stability, and preliminary tribological behavior, and promising results have been observed that give a solid foundation for realistic and valuable application-specific product development [1, 2]. Now the challenge is to experiment further with this concept to apply the underlying science in investigating the feasibility of nanolubricant application for preferred and

versatile materials that are of importance to the Navy and currently used in the lubricant industry.

The findings from NanoMech's preliminary studies are of significant importance in the development of active nanoparticle-based lubricants for mechanical parts and devices, showing outstanding lubrication properties under extreme pressure (EP) and related transient high temperature conditions where boundary layer lubrication is crucial [3], using an environmentally acceptable chemistry..

Devices for energy transfer such as gears, pins, shafts and others inevitably involve mechanical motion, which in turn entails varying degrees of contact and interaction between different types of surfaces, often under environments of extreme-pressure and high-load bearing stresses. An unavoidable consequence of contact between moving surfaces is a force resisting this relative motion - friction. There are two aspects that warrant special attention in this regard: first, mechanical applications are rapidly advancing in a direction that requires machinery to operate at higher loads, speeds and temperatures and often in extremely hostile conditions; and second, greater savings in cost and materials can be achieved through improved lubrication.

To combat the harmful effects of wear and friction, contact surfaces are provided with lubrication. Most lubricants nowadays incorporate one or more additives in order to enhance specific chemical or physical properties. The action of such additives is required when high loads or low speeds disrupt or fail to maintain the hydrodynamic film and boundary lubrication is ushered in. Under boundary lubrication conditions, asperities are no longer separated by a lubricant film and are forced to engage non-elastically. The lubricant additives step in to form a film that forestalls adhesion and lowers wear rate considerably. One such additive that has shown significant promise based on early feasibility testing is a multicomponent colloidal nanolubricant additive that can perform multiple functions, offering extreme pressure lubrication, reduction in the coefficient of friction, and reduced wear under boundary lubrication conditions. The goal in developing the nanolubricant was to provide a platform for producing additive systems for lubricants that will (1) reduce wear, lower friction and improve efficiency and durability of equipment, (2) minimize sulfur and phosphorus content and also lower ash forming elements, and (3) provide an advanced lubrication technology that is friendlier to the environment.

Project Objectives

The high-level objective of this project is to develop nanoparticle-based additives to improve friction and wear characteristics of naval components and systems with a focus to enhance durability and energy efficiency, reduce maintenance costs, and improve environmental sustainability.

For this project, NanoMech is performing following technical tasks that are based on the overall project research plan (see Appendix, Table A1):

1. Design of application-specific active nanolubricants;
2. Synthesis, de-agglomeration, and optimization of nanolubricant;
3. Structural, chemical, and physical analysis of nanolubricant;
4. Tribological testing of nanolubricant.

Project Scope

In the third project quarter, the developed formulations (see first and second quarter reports) were compared to distinguish the effects of these unique additives in providing reduced friction and wear and evaluate their tribological performance. The best-performing candidates were selected and characterized using a number of analytical techniques.

The Design of Experiments approach was used for parameter optimization and scale-up of the process used to synthesize multi-component nanoparticle additive systems for oils and greases. Extensive laboratory-based tribological evaluation of nanomaterials was performed to evaluate friction and wear characteristics in the boundary lubrication regime using Block-on-Ring, Pin-on-Disc, 4 Ball and Extreme Pressure 4 Ball tests. Following this laboratory tribological testing, the performance of the nanolubricant additives will be evaluated in military certified oils using Wedeven Associates' WAM Scuffing Load Capacity Tests in the next project quarter.

Physical and chemical characterization of the additives was performed using a range of microscopic and surface analytic tools (TEM, EDX, XRD, and SEM). The focus was on understanding the inorganic-organic interface chemical behavior resulting in surface lubrication, dispersion of the additives in the hydrocarbon media, and formation of tribofilms at the friction points. Specimens from tribotesting were collected and used for tribofilm analysis. The analysis was carried out in part in the Physics Department and Materials and Manufacturing Research Laboratories (University of Arkansas in

Fayetteville) and in the Frederick Seitz Materials Research Laboratory Central Facilities (University of Illinois in Urbana-Champaign) which are partially supported by the U.S. Department of Energy under grants DE-FG02- 07ER46453 and DE-FG02-07ER46471.

Major Activities

The research activities as outlined in the project plan (Table A1, Appendix) for the funding phase November 12, 2009 – November 11, 2010 and no-cost extension November 12, 2010 - May 12, 2011 re noted below. The major activities of the project are summarized below:

Task 1. Designing of application-specific active nanolubricant (*Timeline for Task 1: November 2009 – August 2010*);

Task 2. Synthesis, de-agglomeration and optimization of nanolubricant (*Timeline for Task 2: January – August 2010*);

Task 3. Structural, chemical and physical analysis of nanolubricant (*Timeline for Task 3: March – November 2010*);

Task 4. Tribological testing of nanolubricant (*Timeline for Task 4: March – October 2010*). Six months no-cost extension was requested and approved to investigate the effects of nanolubricants addition into regular military gear oil and their tribological performance using WAM test, and let the University of Arkansas subcontract team finish the FZG setup (*November 2010 – May 2011*)

Specific tasks with timeline for deliverables and milestones to be performed by NanoMech including tasks for the University of Arkansas as a subcontractor and their progress are described below.

Task 1: Designing of application-specific active nanolubricant

(Timeline for Task 1: November 2009 – August 2010)

In this task, the project team has already designed the application-specific active nanolubricant that contains inorganic nanoparticles integrated with organic molecular medium to add additional lubrication properties and form protective capping layer to suspend them in base oil medium and protect from sedimentation.

The open-ended ellipsoidal architecture of the nanoparticles prepared by lab scale mill, as seen from the images below (Figure 1), provides for inter-planar slippage, exfoliation and ability to supply reactive transfer films on the mating surfaces, thus protecting the underlying substrate from wear and seizure. Nanoparticles form the inorganic core/carrier integrated with phosphorus-based compounds or environmentally benign vegetable oil/phospholipid molecules in a stable surface stabilized composition.

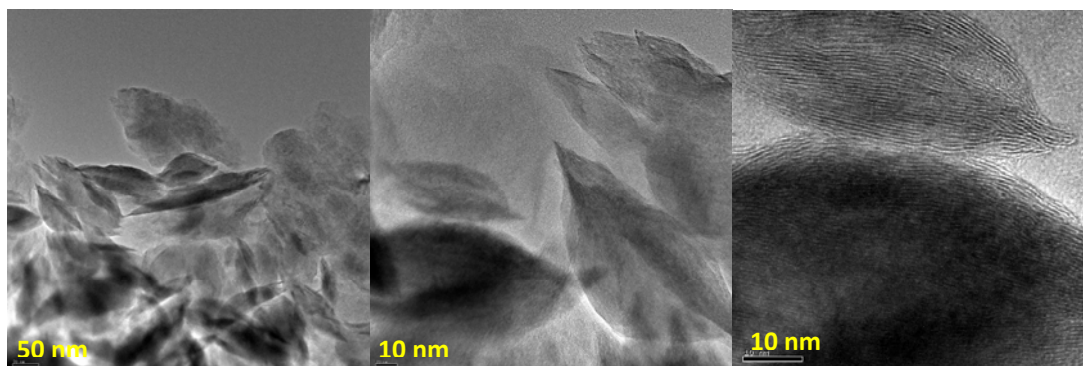


Figure 1. HRTEM images of the nanolubricant

The initially prepared two formulations based on nanoparticles with a capping layer of EP additive and/or vegetable oil and dispersant (see 2nd quarter report) were evaluated for lubrication applications (additives to gear and motor oils and greases) and were used as a base for formulation modification and improvement. In the 3rd quarter, modified formulations were prepared in the same way as the initial formulations, but additional chemistries were added during chemo-mechanical milling to increase their lubrication performance and address specific applications in gear oils and greases. The modified nanolubricants were characterized and compared with the two initially prepared formulations. For details on the observed morphological properties of the modified formulations see Task 3 of this report, and for a comparison of their tribological performance please see Task 4 of this report.

Deliverables

Accomplished deliverables:

1. Design of application-specific active nanolubricants of interest to the Navy and potential Navy customers/collaborators;

2. Materials for synthesis of nanoparticles selected for application as additives in gear oils and greases;
3. Synthesis and optimization of the developed nanolubricant formulations at the lab scale;
4. Structural, chemical, and physical analysis of the developed nanolubricant formulations (see Task 3 for more details).

Task 2: Synthesis, de-agglomeration, and optimization of nanolubricant

(Timeline for Task 2: January – August 2010)

The interaction plots (Figures 2-5) of selected parameters helped to understand interactions between these parameters for the chemo-mechanical process to produce nanoparticles for nanolubricant.

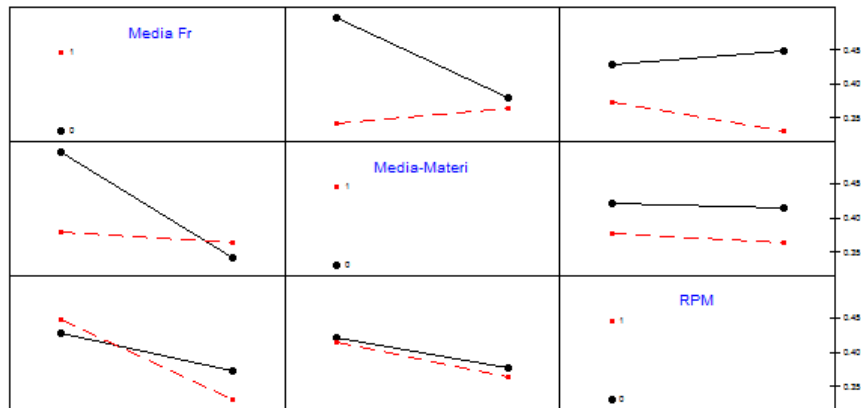


Figure 2. Interaction plot Particle Size by number vs. Media fraction, Media-Material ratio, and RPM

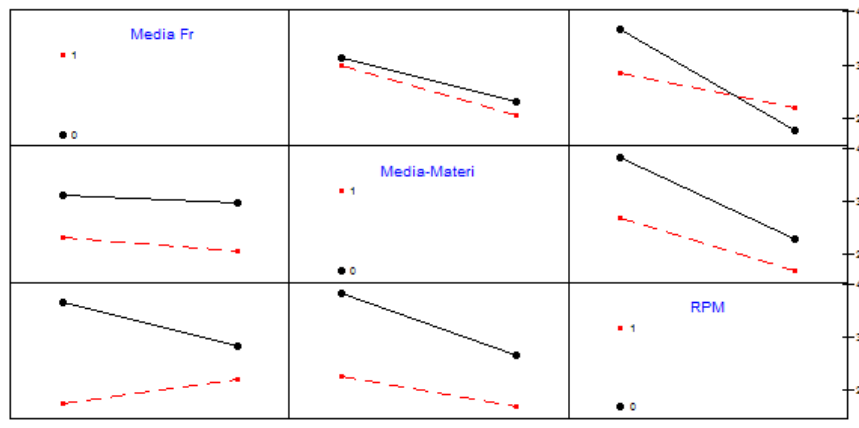


Figure 3. Interaction plot Particle Size by volume vs. Media fraction, Media-Material ratio, and RPM

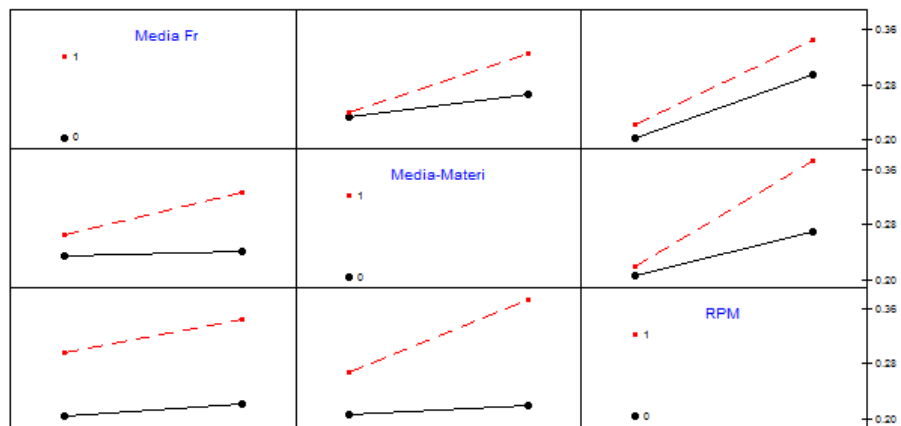


Figure 4. Interaction plot Crystallites vs. Media fraction, Media-Material ratio, and RPM

Additionally, particle size analysis was used to study particle size distribution and agglomeration. Details are presented in Task 3 of this report. Particle size analysis showed the formation of primary and secondary particles (agglomerates).

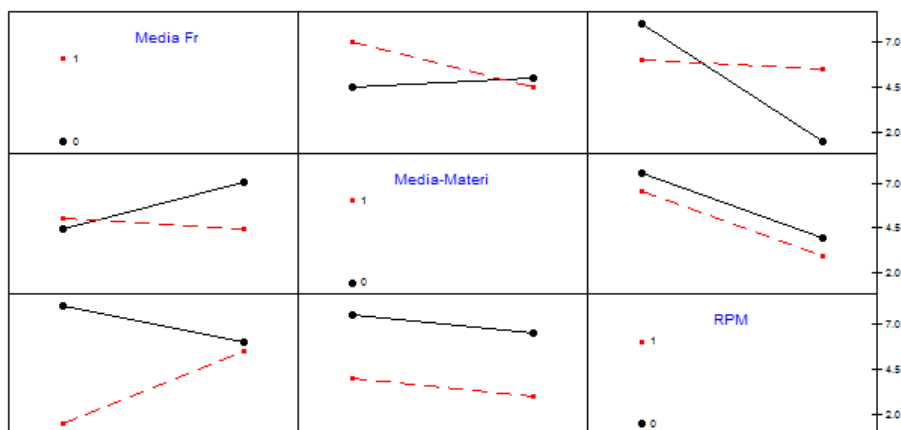


Figure 5. Interaction plot TEM size/shape/dispersity by volume vs. Media fraction, Media-Material ratio, and RPM

Based on the analysis of interactions between synthesis parameters and results from characterization of prepared nanoparticles and combining optimal parameters with optimal time of milling, the final process parameters will be selected in the next project quarter.

Using parameters from design of experiments and applying them for lab-scale and larger-scale processing equipment at NanoMech to perform the synthesis of nanoparticles, the samples were analyzed toward preparation of uniform, non-agglomerated particles with narrow size distribution and optimal process time.

Results and discussions

For process optimization, the solid lubricant powder was chemo-mechanically milled for various time durations. The oil medium in the selected combination was chosen to allow (a) homogeneous dispersion of particles inside the milling space, thus avoiding particle clogging (b) utilizing mechanical energy to forge interaction between solid and organic agents to provide capping and integration of organic molecules in nanoparticles and (c) capping with organic molecules, reduced agglomeration, and preparing a uniform dispersion with the base oil.

In this project period, two nanolubricant formulations with the same composition prepared in lab-scale and larger-scale mills and dispersed in commercially available formulated gear oil and compared along with the oil by itself. The purpose of this comparison was to investigate whether the nanoparticles prepared in larger-scale can be

prepared with less processing time (one sixth, one fourth, one third, or half of lab mill processing time) using optimized parameters of milling. With the comparison of these two samples and the formulated oil by itself, it will be possible see how well our product can work with oils to better the overall task of enhancing lubrication. The morphological comparison of these oils is presented in this task, and tribological comparison is done in the next task through two different types of tribology testing using Pin-on-Disk (POD) and Block-on-Ring (BOR) tests. With these comparisons it can be determined whether the same morphological and tribological properties for nanolubricant prepared in lab-scale mill can be achieved with the larger-scale mill.

Figure 6 shows the sample prepared using the larger-scale mill with 1/6 the processing time of the lab-scale mill. It is clear that significant fracturing of the bulk occurred, but it was not enough to form uniform ellipsoidal nanoparticles with sizes similar to lab mill prepared samples (Figure 1). Particle size analysis (Table 1) also confirms the presence of large size particle fraction (by volume) and still comparatively high mean size of prepared nanoparticles (by number).

The increase of processing time to 1/3 the length of initial lab-scale milling time (Figure 7 and Table 2) and to 1/2 length of initial lab scale milling time (Figure 8 and Table 3) showed a consistent decrease in nanoparticle sizes and formation of ellipsoidal particles.

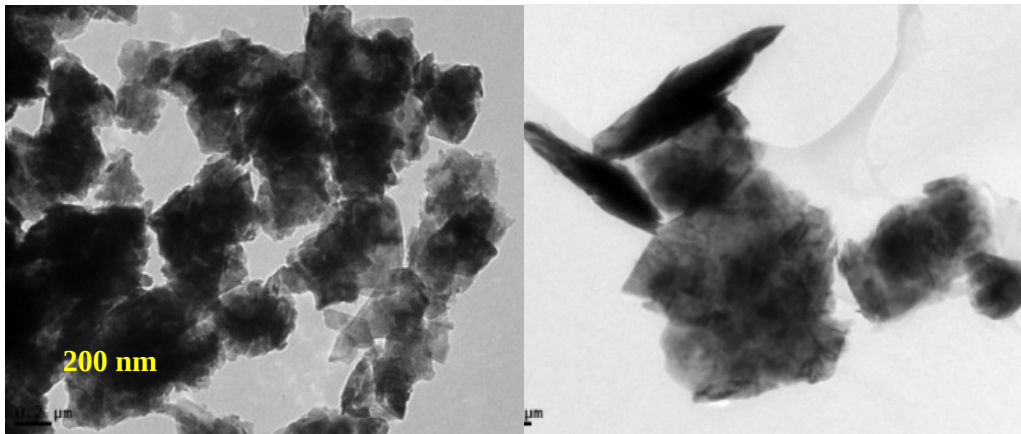


Figure 6. TEM of sample prepared by larger-scale mill (1/6 of initial processing time)

Table 1. PSA of sample prepared by larger-scale mill (1/6 of initial processing time)

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			0.48080 μm	0.38384 μm	0.2778 μm
NG1D2ZX	10	50	90			
	0.2096 μm	0.3838 μm	0.8754 μm			

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1.48148 μm	1.25747 μm	1.2322 μm
NG1D2ZX	10	50	90			
	0.5806 μm	1.2575 μm	2.6898 μm			

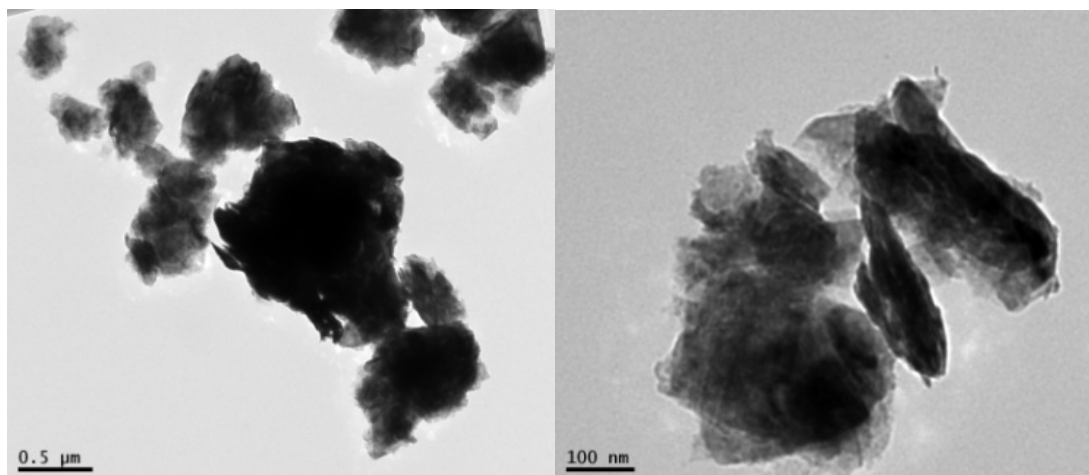


Figure 7. TEM of sample prepared by larger-scale mill (1/3 of initial processing time)

Table 2. PSA of sample prepared by larger-scale mill (1/3 of initial processing time)

Particle Size Analysis	Distribution Base: Volume			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			1.31654 μm	1.05313 μm	1.0734 μm
NG1D2ZX	10	50	90			
	0.4457 μm	1.0531 μm	2.5216 μm			

Particle Size Analysis	Distribution Base: Number			Mean Size	Median Size	Mode Size
	Diameter on Cumulative %			0.39299 μm	0.31964 μm	0.2765 μm
NG1D2ZX	10	50	90			
	0.1863 μm	0.3196 μm	0.6955 μm			

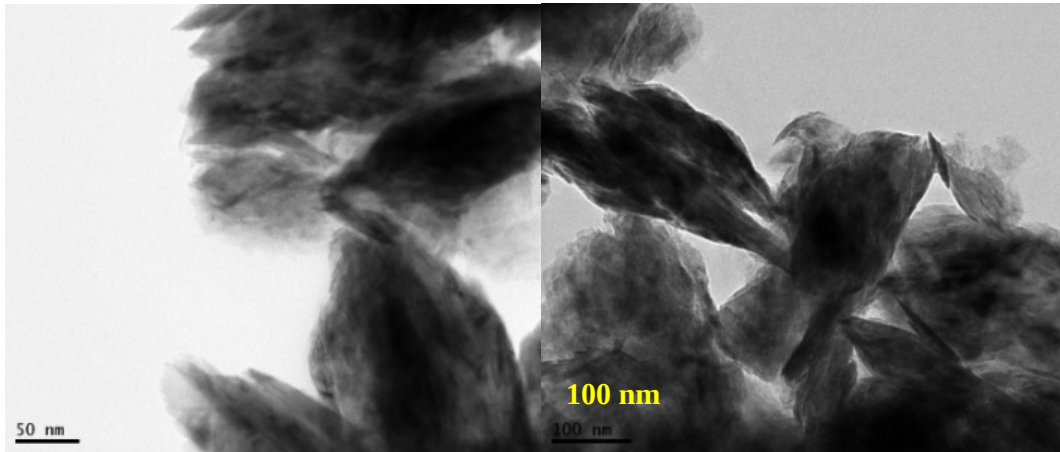


Figure 8. TEM of sample prepared by large scale mill (1/2 of initial processing time)

Table 3. PSA of sample prepared by large scale mill (1/2 of initial processing time)

Particle Size Analysis		Distribution Base: Volume			Mean Size	Median Size	Mode Size
		Diameter on Cumulative %			1.21562 um	0.89820 um	0.9372 um
NG1D2ZX	10	50	90				
	0.3498 um	0.8982 um	2.4557 um				

Particle Size Analysis		Distribution Base: Number			Mean Size	Median Size	Mode Size
		Diameter on Cumulative %			0.32721 um	0.27283 um	0.2425 um
NG1D2ZX	10	50	90				
	0.1669 um	0.2728 um	0.5527 um				

The prepared sample (Figure 8) showed similar structural and morphological characteristics of the nanoparticles as compared to samples prepared using the lab mill. The runs of 2/3 the length of the initial processing time were also performed to determine whether 1/2 the length of the initial processing time is sufficient, it was found that longer milling time was not effective to achieve a further significant improvement in particle sizes de-agglomeration in comparison with shorter runs. It was postulated that 1/3 of initial processing time for sample preparation by larger-scale mill is optimal for the scale-up process and these time parameters were used in standard operation procedures (SOP) for

Accomplished Deliverables

1. Design of experiments for synthesis and optimization for scale up;
2. Development of nanolubricant production procedure;
3. Synthesis of nanolubricants for naval applications;
4. Product Control Procedures (SOP) are developed.

Task 3: Structural, chemical, and physical analysis of nanostructures and inorganic-organic interfaces (Timeline for Task 3: March – October 2010)

Complementary analytical techniques are applied with particular objectives to study properties of synthesized nanoparticles and scale-up optimization (size and shapes, surface area, nanostructure, and chemical analysis) and tribological performance (tribofilm formation, debris formation, nanoparticles morphology). The structural analysis (size and shapes of nanoparticles) was discussed in the previous task in combination with scale-up discussions. This task covers chemical and physical analysis of nanostructures and the inorganic-organic interface in gear oils and greases, and analysis of formed tribofilms after the tribotesting.

3.1. Nanolubricant additives for oil

The initial two formulations of the nanolubricant were modified and improved for specific application as additives for gear oils and greases. The components of the nanoparticle additives in gear oil are encoded as follows (numbers in the sample identifications are for unique identification only and do not denote how much of any component was added to the formulation):

Table 4. Modified nanolubricant formulations prepared for gear oil

GY1:	Friction modifier Y (FM)
GT2:	High temperature extreme pressure additive T (HT-EP)
GO3:	Blank Gear Oil (GO)
GXYZ4:	Friction modifier Y, Phospholipid X, EP additive Z (EP)
GTWX5:	HT-EP T, Vegetable oil W (VO), Phospholipid X (PL)
GTYZ6:	HT-EP T, FM Y, EP Z
GZU17:	EP Z, Dispersant U1
GU2Z8:	EP Z, Dispersant U2
GZX9:	Initial formulation 1 of nanolubricant
GZ10:	EP Z
GV11:	Initial formulation 2 of nanolubricant

The prepared modified formulations for greases were analyzed using Particle Size Analysis (Table 5) and their tribological performance was studied using Pin-on-Disk and Block-on-Ring tribometers (see Task 4). The Particle size analysis was used to select samples with the smallest sizes of primary nanoparticles and smallest sizes of secondary particles (agglomerates).

Table 5. PSA of Modified nanolubricant Formulations

Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GY1			Diameter on Cumulative %			1490 nm	729 nm	477 nm
			10	50	90			
			313 nm	729 nm	3310 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GY1			Diameter on Cumulative %			327 nm	290 nm	277 nm
			10	50	90			
			190 nm	290 nm	500 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GYZ12			Diameter on Cumulative %			916 nm	585 nm	318 nm
			10	50	90			
			230 nm	585 nm	2020 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GYZ12			Diameter on Cumulative %			238 nm	207 nm	184 nm
			10	50	90			
			140 nm	207 nm	366 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GXYZ13			Diameter on Cumulative %			1500 nm	1100 nm	1230 nm
			10	50	90			
			329 nm	1096 nm	3212 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GXYZ13			Diameter on Cumulative %			263 nm	216 nm	184 nm
			10	50	90			
			140 nm	216 nm	432 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GXYZ4			Diameter on Cumulative %			2390 nm	1550 nm	1410 nm
			10	50	90			
			470 nm	1550 nm	5420 nm			

Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GXYZ4			Diameter on Cumulative %			303 nm	237 nm	185 nm
			10	50	90			
			153 nm	237 nm	524 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GT2			Diameter on Cumulative %			606 nm	429 nm	278 nm
			10	50	90			
			190 nm	429 nm	1240 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GT2			Diameter on Cumulative %			203 nm	179 nm	161 nm
			10	50	90			
			125 nm	179 nm	306 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GTX4			Diameter on Cumulative %			1160 nm	667 nm	363 nm
			10	50	90			
			247 nm	667 nm	2790 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GTX4			Diameter on Cumulative %			243 nm	214 nm	185 nm
			10	50	90			
			144 nm	214 nm	372 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GTWX5			Diameter on Cumulative %			1350 nm	832 nm	821 nm
			10	50	90			
			272 nm	832 nm	3060 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GTWX5			Diameter on Cumulative %			266 nm	223 nm	185 nm
			10	50	90			
			144 nm	223 NM	429 nm			
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size
GTYZ6			Diameter on Cumulative %			703 nm	443 nm	276 nm
			10	50	90			
			179 nm	443 nm	1550 nm			
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size
GTYZ6			Diameter on Cumulative %			193 nm	170 nm	159 nm
			10	50	90			
			121 nm	170 nm	287 nm			

Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			1340 nm	1020 nm	1230 nm	
GU1W14			10	50	90				
			295 nm	1020 nm	2810 nm				
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			248 nm	202 nm	162 nm	
GU1W14			10	50	90				
			135 nm	202 nm	405 nm				
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			2350 nm	1790 nm	1620 nm	
GU1Z7			10	50	90				
			628 nm	1790 nm	4840 nm				
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			332 nm	237 nm	162 nm	
GU1Z7			10	50	90				
			149 nm	238 nm	641 nm				
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			2200 nm	1830 nm	1850 nm	
GU2W15			10	50	90				
			782 nm	1830 nm	4150 nm				
Particle Size Analysis			Distribution Base: Volume			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			502 nm	365 nm	197 nm	
GU2W15			10	50	90				
			197 nm	365 nm	992 nm				
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			1790 nm	1410 nm	1610 nm	
GU2Z8			10	50	90				
			442 nm	1410 nm	3700 nm				
Particle Size Analysis			Distribution Base: Number			Mean Size	Median Size	Mode Size	
			Diameter on Cumulative %			322 nm	257 nm	241 nm	
GU2Z8			10	50	90				
			160 nm	257 nm	555 nm				

In general, almost all modified formulations had nanoparticles with similar morphological characteristics to nanoparticles from the initial formulations. However, several of the samples with the modified formulations showed significant improvement in

achieving smaller sizes of nanoparticles (Table 5, samples GYZ12, GT2, GTYZ6) and less aggregated secondary particles (samples GYZ12, GT2, GTYZ6).

3.2. Nanolubricant additives for grease

NanoGlide nanoparticles were used as an additive for greases and their structural and tribological properties were studied (Four Ball Test).

Two different formulations of the nanolubricant additive (1 ZX and 2 WX) were used as additives in extreme pressure lithium-base grease (EP Li-base grease) for comparison with performance of neat base grease and base grease formulated with commercially available MoS_2 (micron size nanoparticles) and commercially available WS_2 nanoparticles. Concentration of all additives was kept constant in terms of weight percentage of the solid phase.

3.2.1 Morphological and compositional analysis of grease tribofilms through Scanning Electron Microscopy (SEM)/ Energy-dispersive X-ray spectroscopy (EDX)

The 4 Ball wear test is the predominant wear tester used to study the chemical interactions occurring at wearing contacts for greases. The wear tracks generated on one of the stationary balls from the 4 Ball wear test were observed under the Nova SEM.

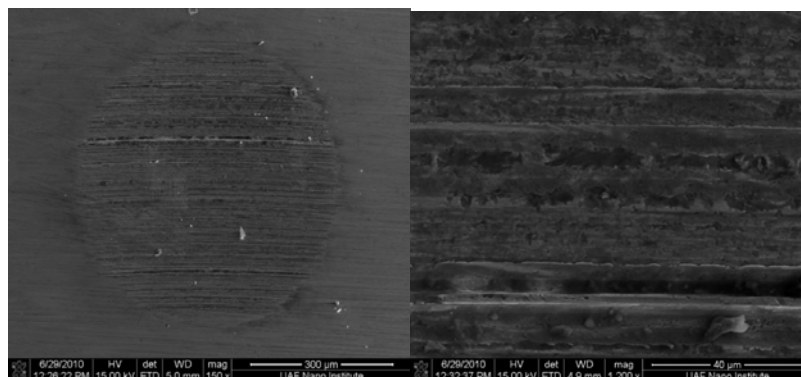


Figure 9. SEM of wear for base grease 4 Ball test

As can be observed below, the wear track showed presence of grooves running parallel to the direction of sliding, plastic flow, and fine wear debris, all indicative of the occurrence of abrasive wear. There is some pull-out seen on the track suggesting that some adhesive wear could have taken place at regions where the tribofilm was formed insufficiently or

was weakly adherent to the surface. The EDX analysis shows the elemental composition of EP Li-base grease (Figure 10) that was used as a base grease for nanolubricant additives.

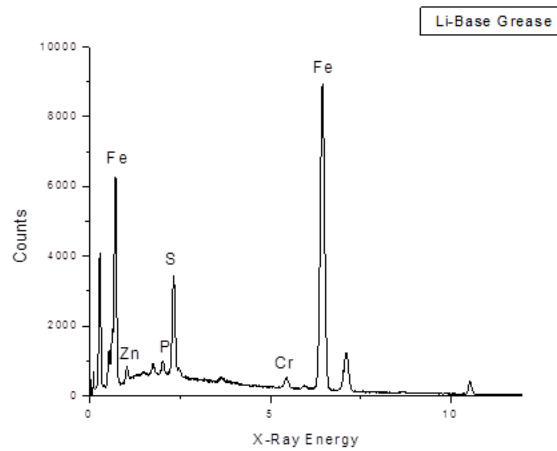


Figure 10. EDX spectrum of wear for EP Li-base grease using 4 Ball test

From the elemental maps, the distribution of elements on the tribofilm can be seen. The film formed through the base grease shows the presence of phosphorus and sulfur. The presences of these elements were also confirmed through the EDX spectrum. These elements are main components of extreme pressure additives in greases.

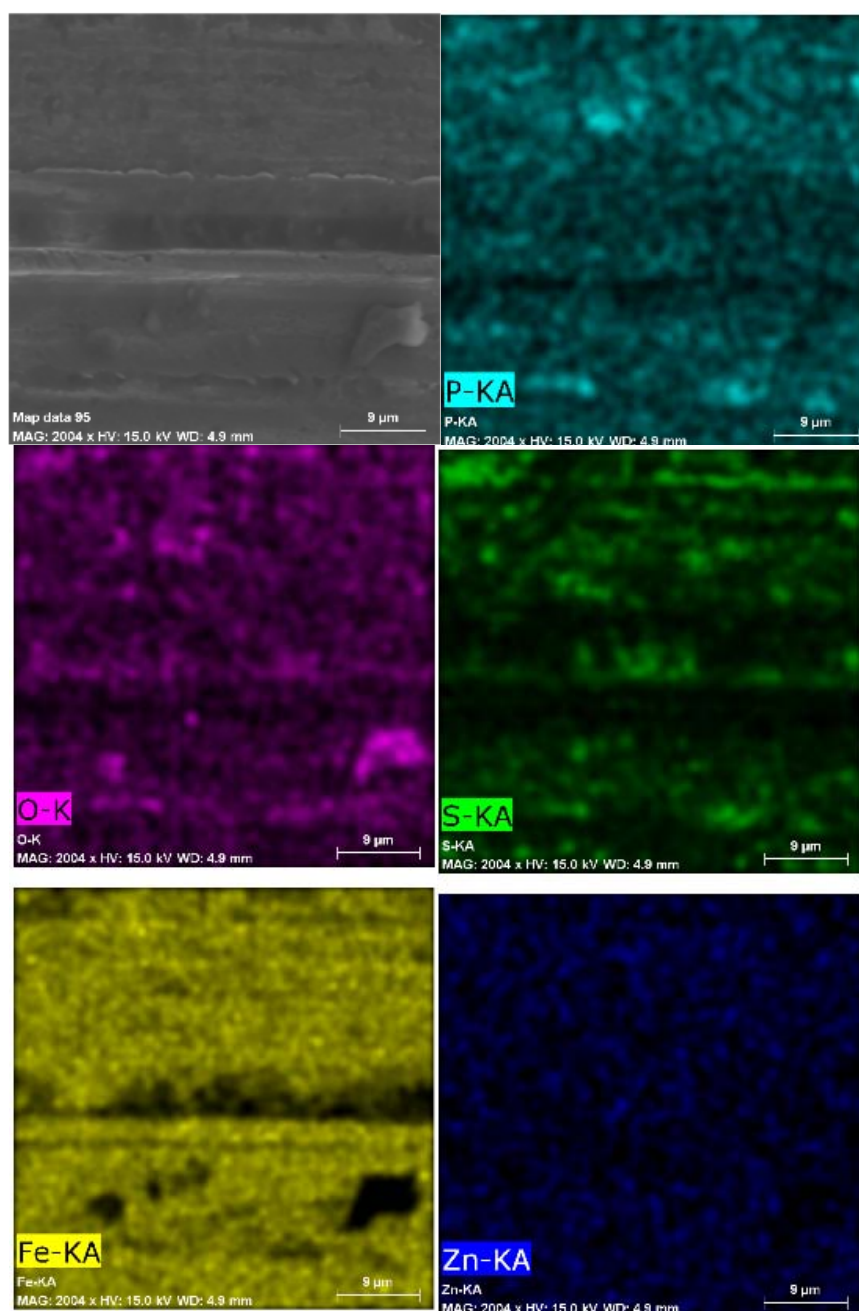


Figure 11. SEM and EDX elemental mapping (phosphorous, oxygen, sulfur, iron and zinc) of wear region for base grease 4 Ball test

Base grease was formulated with commercially available molybdenum sulfide powder from bulk using the same weight percentage of solid phase as was used for greases formulated with nanoparticles. From the images above, it can be concluded that wear occurred mostly through abrasion. At some regions pull-out of the tribofilm can be seen

suggesting that either the tribofilm was incompletely formed or was weakly bonded to the substrate.

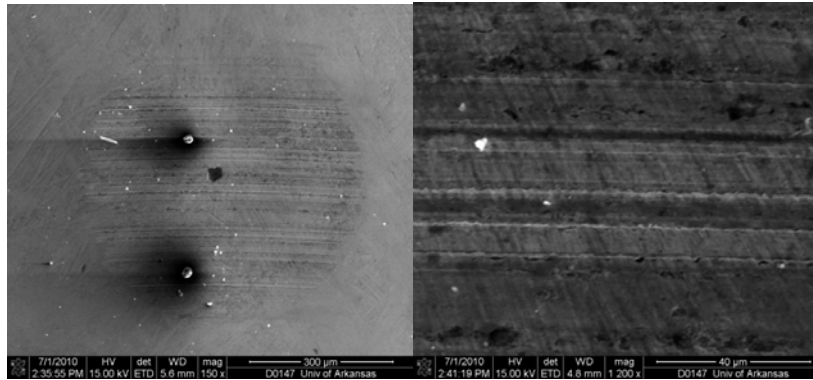


Figure 12. SEM of wear for base grease and MoS₂ microparticles 4 Ball test

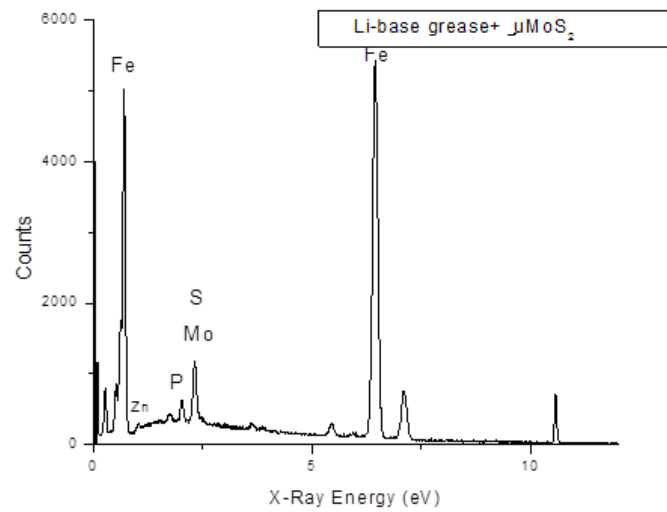


Figure 13. EDX spectrum of wear for EP Li-base grease with MoS₂ microparticles using 4 Ball test

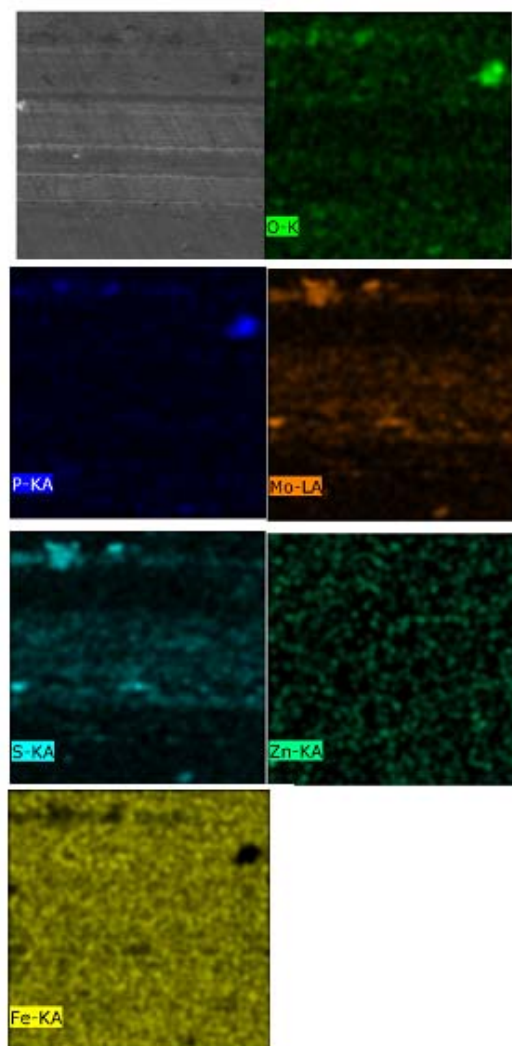


Figure 14. SEM and EDX elemental mapping (oxygen, phosphorous, molybdenum, sulfur, zinc, and iron) of wear region for base grease and MoS₂ microparticles 4 Ball test

From the above maps, there can be seen localized distribution of Mo and S suggesting the formation of MoS₂ tribofilms. The occurrence of P and O at similar locations on the tribofilm may suggest the formation of phosphates.

The tribofilms formed for nanolubricant additive 1 ZX in grease showed less abrasive wear, some pull-out, and plastic deformation. There was incorporation of wear debris in the grooves that may provide additional benefit of supporting some part of the load and/or act to help in sliding by acting as miniature ball-bearings.

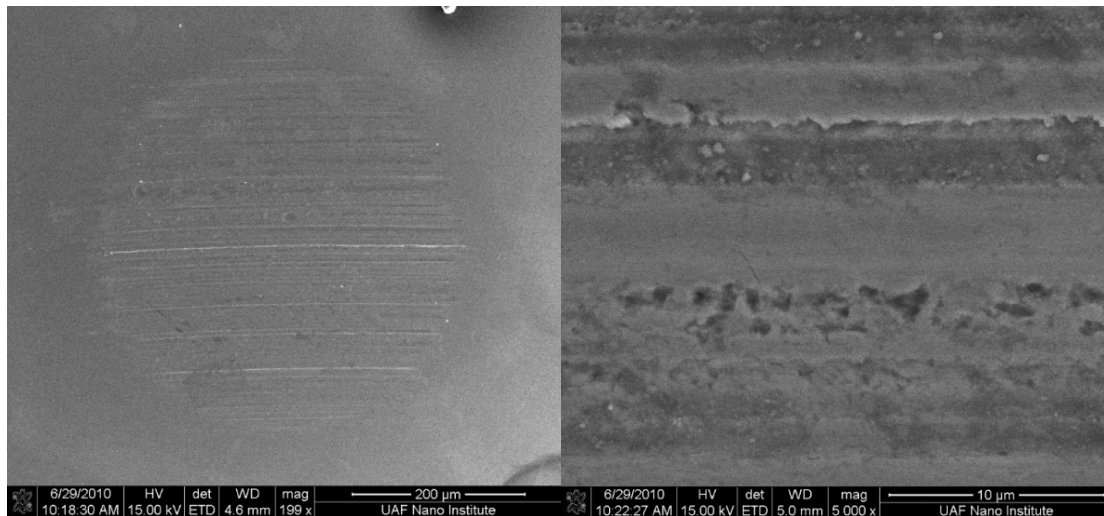


Figure 15. SEM of wear for base grease and nanolubricant additive 1 ZX using 4 Ball test

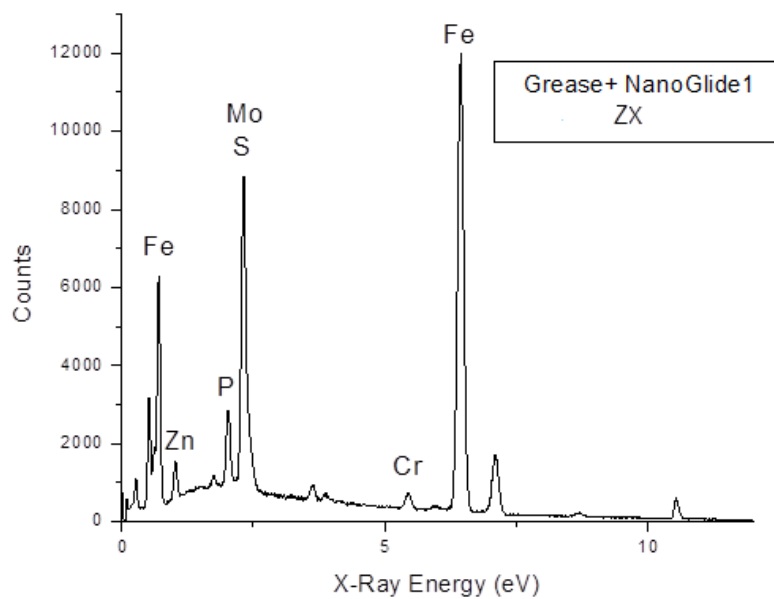


Figure 16. EDX spectrum of wear for EP Li-base grease and nanolubricant additive 1 ZX using 4 Ball test

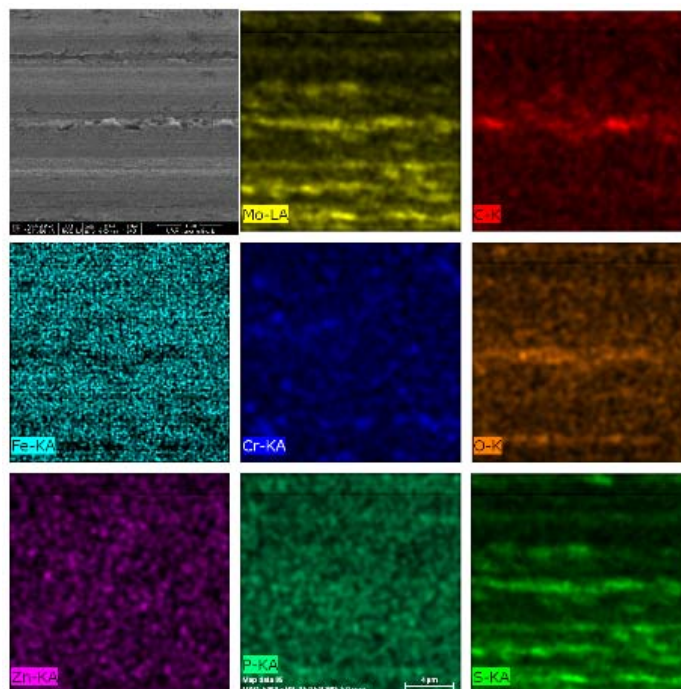


Figure 17. SEM and EDX elemental mapping (molybdenum, carbon, iron, chromium, oxygen, zinc, phosphorous, and sulfur) of wear region for base grease and nanolubricant additive 1 ZX using 4 Ball test

The occurrence of Mo and S at the wear tracks was indicative of the formation of an MoS_2 tribofilm. Not much information is available to draw conclusions on the formation of phosphates or other compounds.

As is observed from the elemental maps, there could be formation of a patchy tribofilm of MoS_2 on the substrate since lesser signals are obtained from Fe in the same regions. There could also be some formation of phosphates since P and O occur at similar locations on the surface.

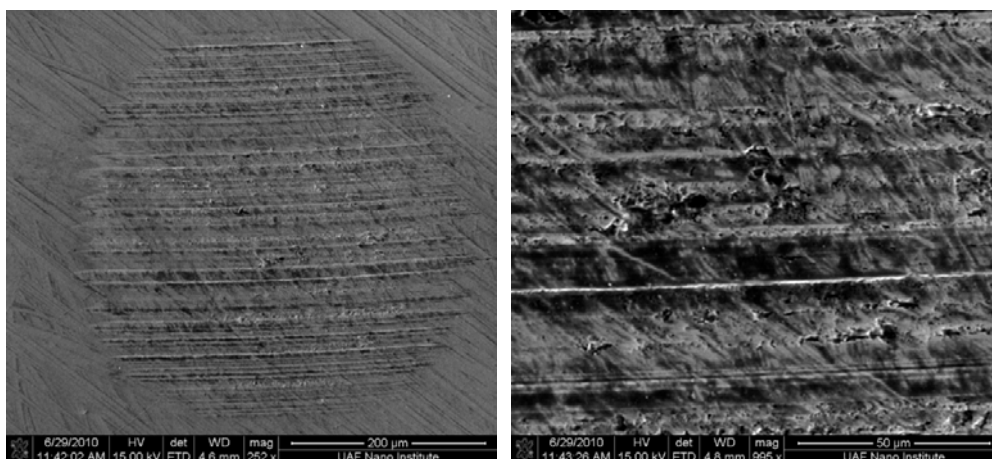


Figure 18. SEM of wear for base grease and nanolubricant additive 1 ZX using 4 Ball test

Shown below are the SEM images of grease containing nanolubricant additive 2 WX. Mild abrasive wear and a few regions of pull-out can be observed. In the cavities formed, there is deposition of either debris or some particles that could help support a part of the load.

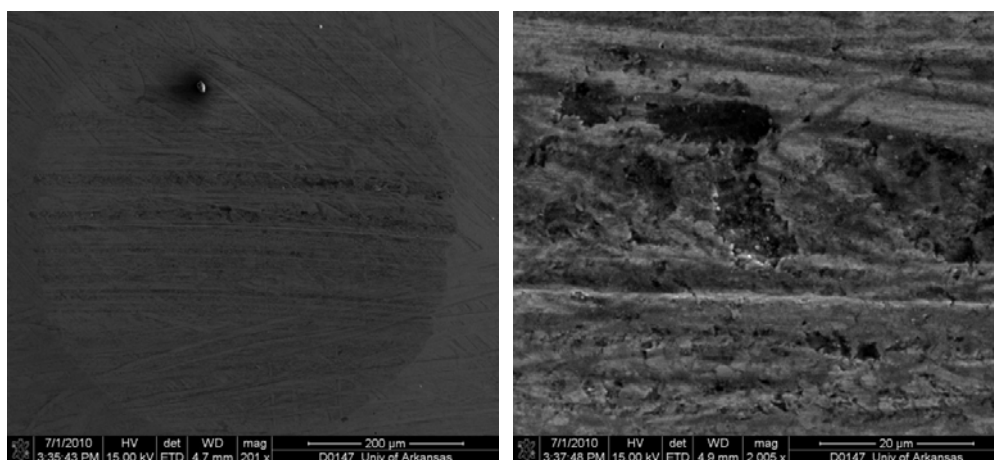


Figure 19. SEM of wear for base grease and nanolubricant additive 2 WX using 4 Ball test

EDS was performed on the area of the tribofilm shown in the inset picture. The Zn from the grease participates in the formation of the tribofilm. The elemental maps below show the distribution of the elements on the tribofilm formed from nanolubricant additive 2 WX.

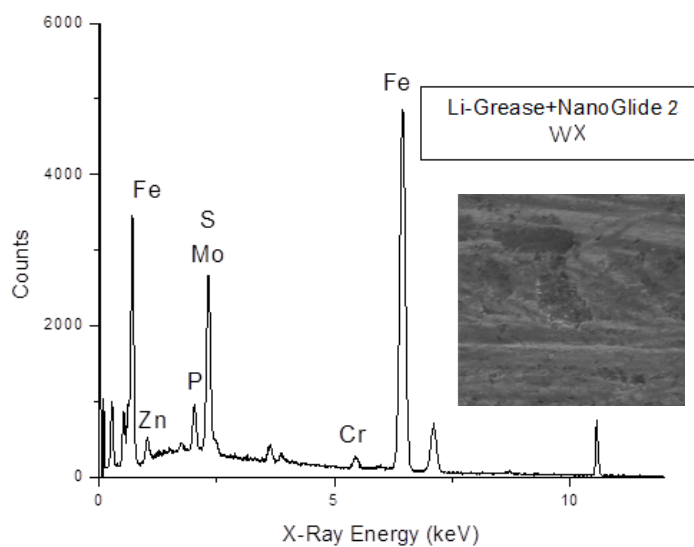


Figure 20. EDX spectrum of wear for EP Li-base grease and nanolubricant additive 2 WX using 4 Ball test

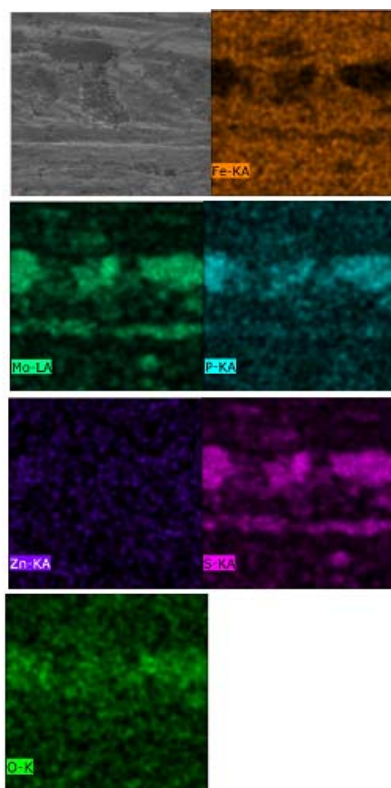


Figure 21. SEM and EDX elemental mapping (iron, molybdenum, phosphorous, zinc, sulfur, and oxygen) of wear region for base grease and nanolubricant additive 2 WX using 4 Ball test

As seen from the elemental maps, in the regions of pull-out cavities, there could be deposition of MoS_2 film and/or phosphates. The lesser signal received from Fe may suggest that there could be less formation of iron compounds in the cavities.

Base grease was formulated with commercially available tungsten sulfide powder from nanoparticles using the same weight percentage of solid phase as with the greases formulated with nanolubricant additive. The SEM wear track indicates that the tribofilm is very patchy with mild abrasive wear and presence of wear debris/ particles in the grooves/ cavities.

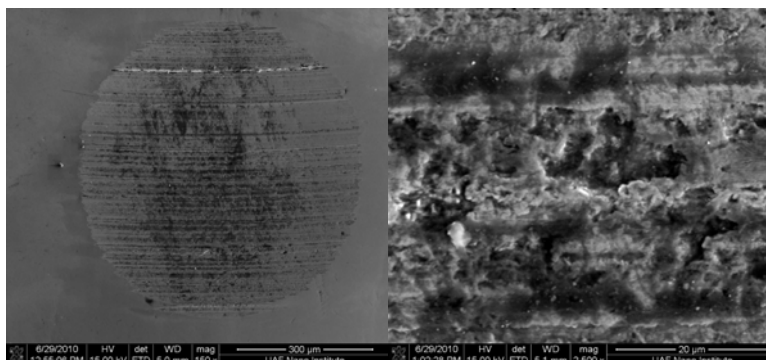


Figure 22. SEM of wear for base grease and WS_2 nanoparticles using 4 Ball test

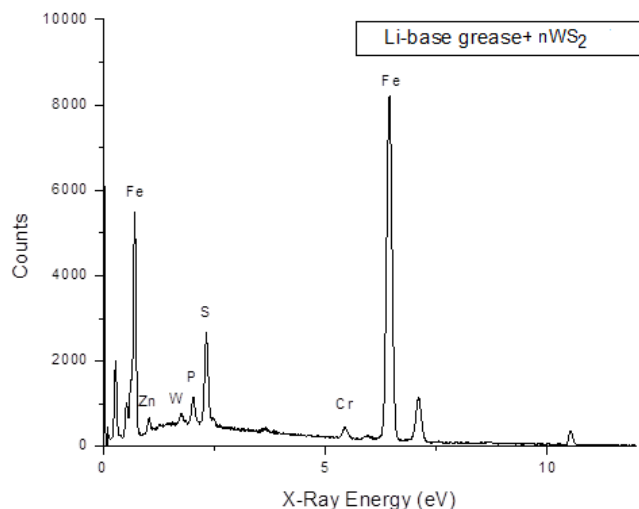


Figure 23. EDX spectrum of wear for EP Li-base grease and WS_2 nanoparticles using 4 Ball test

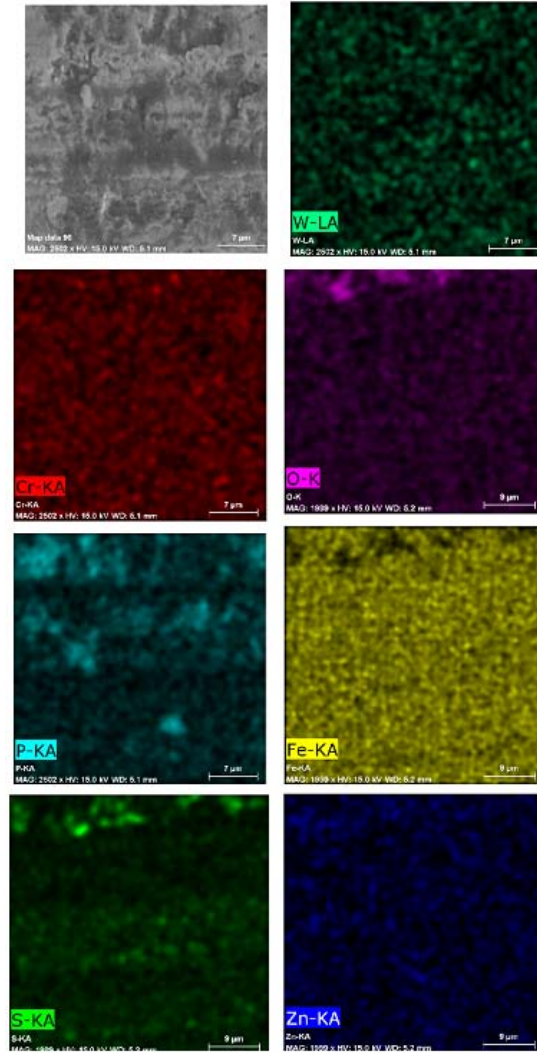


Figure 24. SEM and EDX elemental mapping (tungsten, chromium, oxygen, phosphorous, iron, sulfur, and zinc) of wear region for base grease and WS₂ nanoparticles using 4 Ball test

The elemental maps indicate that there is localized occurrence of phosphorus and sulfur that could be present as phosphates, sulfides, and sulfates. The presence of some amounts of zinc could be from the base grease which contains 5-10% zinc compounds.

Conclusions

Tribofilms from nanolubricant additive 1 ZX and nanolubricant additive 2 WX show mild abrasive wear and that from nanolubricant additive 2 and WS₂ appear patchy with cavities.

Only qualitative information was obtained from the EDS data and to understand the nature of bonding of different elements, further characterization using XPS/Auger techniques may be performed.

Task 4: Tribological testing of nanolubricant

(Timeline for Task 4: March – November 2010, no-cost extension)

Tribological testing was conducted using bench-top tribological test setups (Block-on-Ring, Pin-on-Disc, 4 Ball, and Extreme Pressure 4 Ball tests) focusing on boundary lubrication conditions.

4.1. Tribological performance of nanolubricant in gear oils

The lubrication performance of gear oils and greases with nanoparticle additives was studied through tribological testing. The test results were used to generate friction and wear maps demonstrating the useful tribological performance and to compare performance of nanoparticles in gear oils and greases. The tribological testing and tribofilm analysis were used to understand the behavior of the additives in the oil blend and to develop the final nanoparticles-based formulation for use in the target applications.

Modified nanolubricant formulations were added to gear oils to evaluate and compare their performance. The gear oils were specifically selected to see the direct effect of MoS₂ nanoparticle addition on the formulated oil. Tribological performance of nanoparticles in both gear oils and grease will be reported in this report period.

Block on ring tribotesting

A CETR tribometer model UMT-3 with a Block-on-Ring driver configured for a self-leveling block (SLB) was used for tribotesting. The self-leveling block consisted of a holder for the block to maintain its position, resting on the ring, while a pin modified the load from above.

Each test consisted of a different lubricant and three, consecutively performed steps. The first step, after centering the carriage to press the block, consisted of applying thirty-three kilograms worth of force on the block. Afterwards, the ring was spun at one thousand rpm for a full minute to warm-up and break-in the operating components (ring, block,

driver, etc.). Finally, data for temperature and coefficient of friction (COF) were collected for comparison during the final step: a run at five hundred rpm lasting thirty minutes.

Each graph (Figure 25 and 26) consists of plots labeled according to their formulation (GF refers to formulated gear oil G, GNF refers to non-formulated gear oil (neat), and GNG refers to gear oil formulated with nanolubricant ZX; index 1 refers to the first run and index 2 refers to the second run).

The graphs each consist of raw data from the tribometer that have been reduced through averaging by a factor of one-hundred twenty for the sake of visual representation.

Table 6 summarizes the tribological performance of gear oils - non-formulated (NF) and formulated (F) and formulated gear oil with nanolubricant additive ZX additive (NG). It is clear that gear oil with nanolubricant additive is the leader in smallest coefficient of friction, lowest oil temperature, and smallest wear scar area.

Table 6. Tribological performance of gear oils and nanolubricant ZX

Sample	Average COF, μ	Maximum Temperature, °C	Wear, mm ²
NF	0.126	49.5	6.37
F	0.112	51.3	3.10
NG	0.094	43.2	2.63

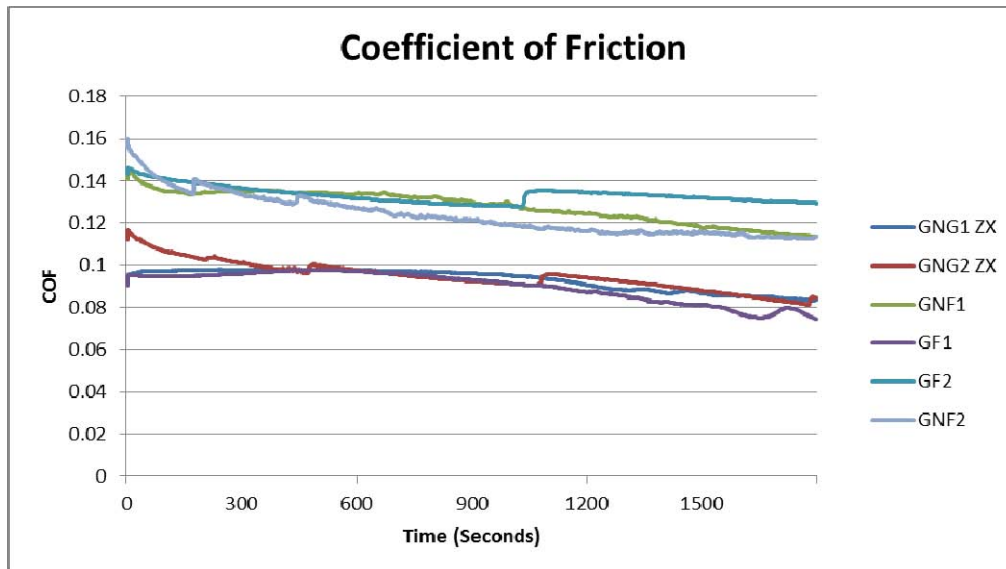


Figure 25. COF comparison for gear oils and nanolubricant additive ZX using Block-on-Ring test

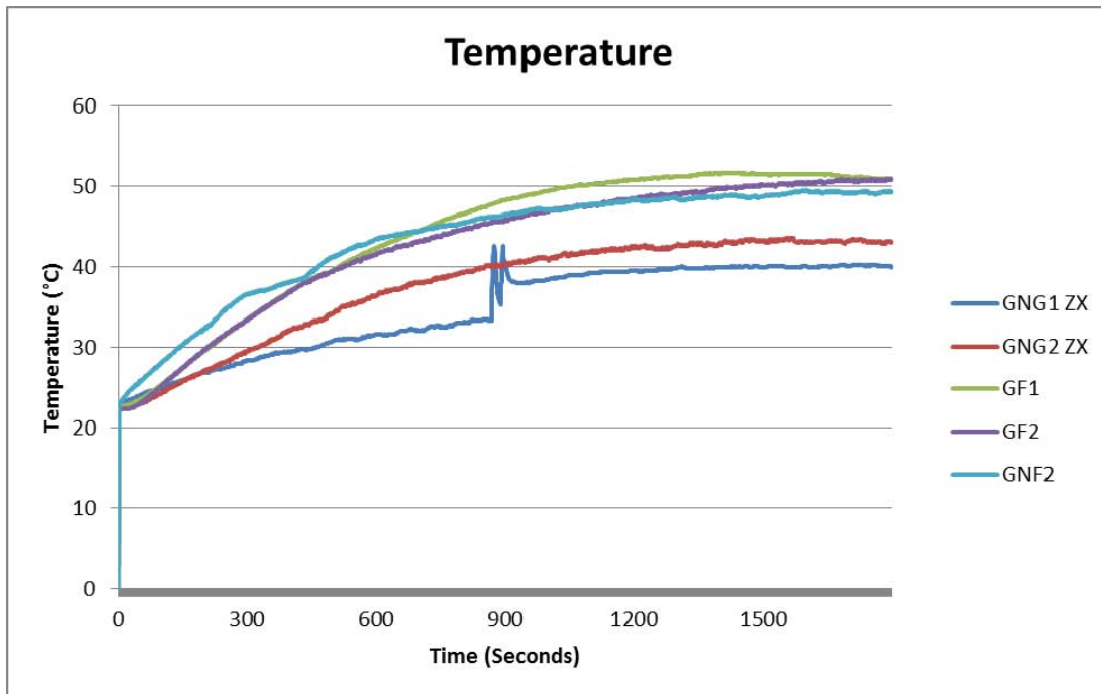


Figure 26. Temperature comparison for gear oils and nanolubricant additive ZX using Block-on-Ring test

Following tribotesting, the blocks were SEM imaged and the surface wear scar was measured using an optical microscope. SEM pictures and microscope pictures were taken of the wear scars to assess how well the blocks were lubricated. The images from the optical microscope are not precise, and further study should be done using a profilometer.

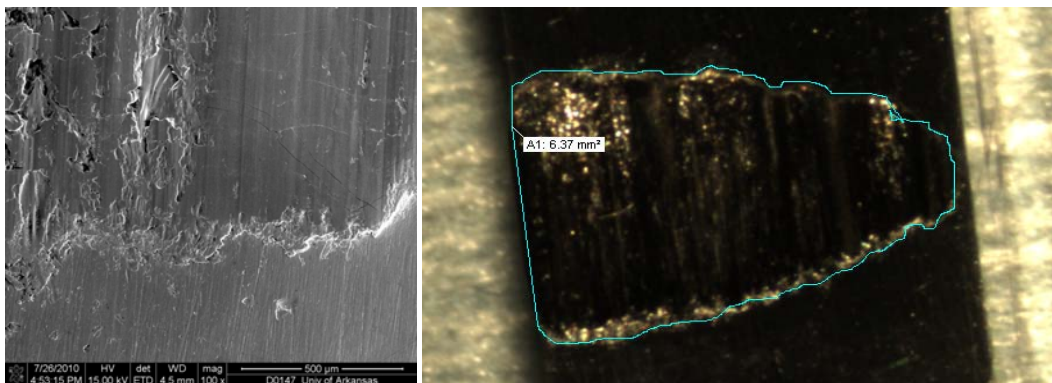


Figure 27. SEM image (left) and optical microscope image with wear surface (right) on block for non-formulated gear oil (NF)

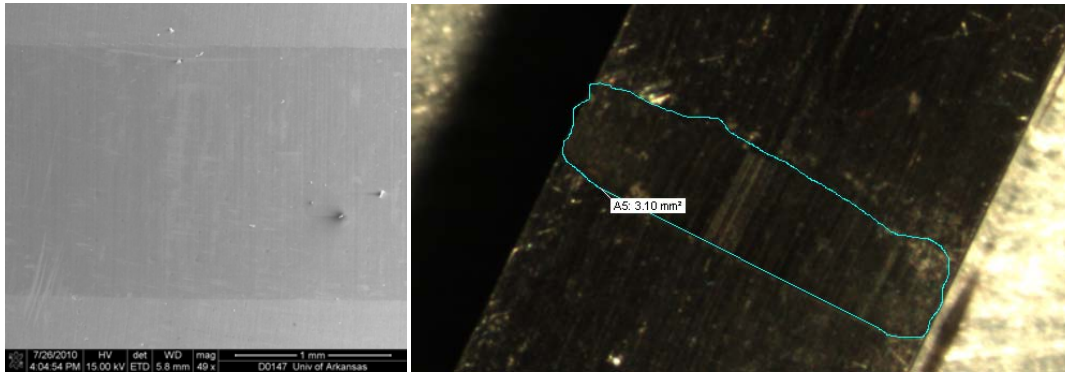


Figure 28. SEM image (left) and optical microscope image with wear surface (right) on block for formulated gear oil

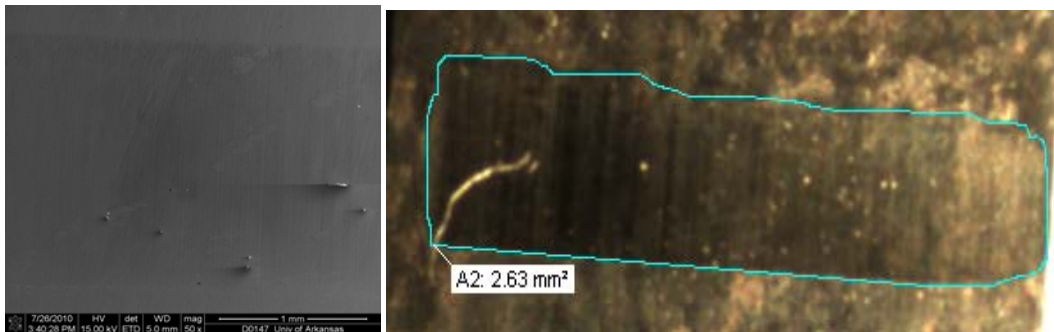


Figure 29. SEM image (left) and optical microscope image with wear surface (right) on block for formulated gear oil with nanolubricant additive ZX (NG)

In terms of reproducibility, the results show very little difference between testing runs for the same samples. This finding, along with the values of standard deviation and average percent difference, indicates good consistency in the test results.

In terms of tribological performance, nanolubricant ZX formulated oils performed best in terms of their coefficient of friction, in oil temperature over time, and measured wear scar area. The wear scar data for all tests was collected by optical microscope measurements, and generally follows and supports the trend in the rest of the data for wear.

The modified formulations of nanolubricant (see section 3.1 and Table 4) were prepared and added to formulated gear oil. Figures 30 and 31 give a good representation of these formulations for lubrication performance and temperature of oils during Block-on-Ring testing. There is correspondence between a higher temperature and a higher coefficient of

friction. This is so because as more wear occurs, the kinetic energy of the interaction is transferred to the surrounding oil.

As a final addendum to the analysis of the Block-on-Ring testing, the surface areas of the wear scars on the blocks were measured from the wear images, which proved to be difficult to read at best. The larger wear scars do seem to correspond with the higher coefficients of friction and temperatures. Therefore, the best formulation is one with the least amount of wear, which would come from the lowest friction and lowest temperature category (e.g., GTYZ6, GU2Z8, and GXYZ4).

Table 7. Tribological performance of gear oil with modified formulations of nanolubricant using Block-on-Ring Test

Samples	COF	Temperature, °C	Surface Wear, mm ²
GY1	0.059	34.3	2.20
GT2	0.062	50.4	2.21
GO3	0.081	51.5	2.84
GXYZ4	0.059	48.3	2.04
GTWX5	0.062	43.1	2.42
GTYZ6	0.071	49.0	2.03
GZU17	0.070	44.4	2.73
GU2Z8	0.057	41.5	2.53
GZX9	0.080	45.3	3.02
GZ10	0.073	52.1	2.79
GV11	0.079	51.2	2.25

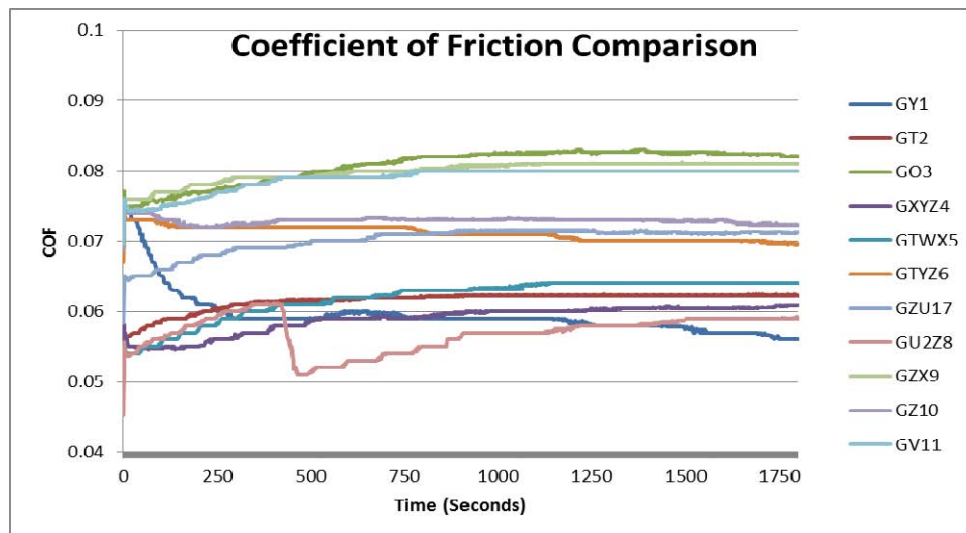


Figure 30. COF comparison for gear oil and modified nanolubricant formulations using Block-on-Ring test

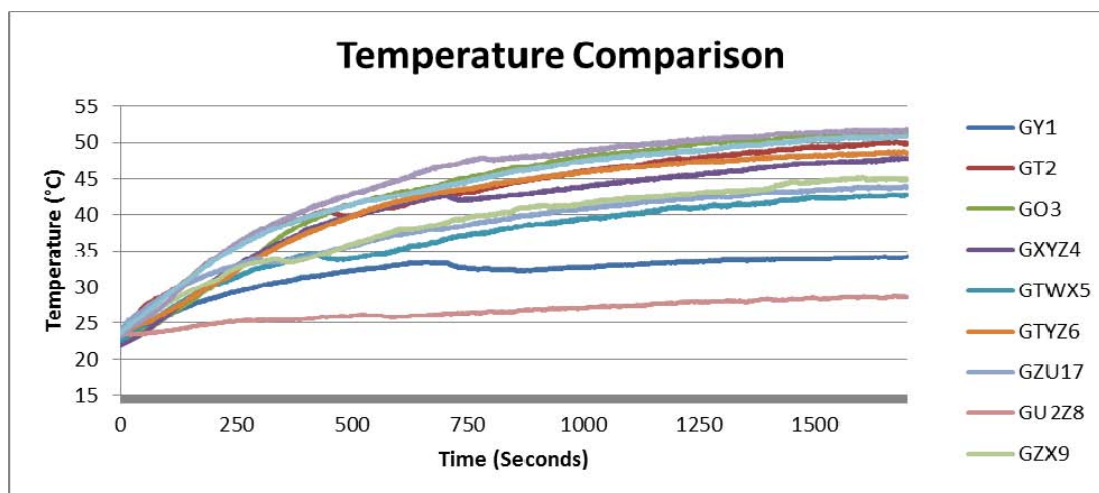


Figure 31. Temperature comparison for gear oil and modified nanolubricant formulations using Block-on-Ring test

Drawing from the results listed above, the most effective formulations with the formulated oil were GY1 and GU2Z8. These two were ranked best because both have the lowest temperature and lowest coefficient of friction readings. In contrast, GO3, GZ10, and GV11 had some of the poorest rankings because they all exhibited high temperatures and high coefficients of friction. Between the two extremes, the only other oils that could be looked into for any more precise results would be GTWX5, GXYZ4, and GT2 since each had either a low final temperature or a low coefficient of friction.

Pin on Disk Testing

Gear oils with modified nanolubricant formulation were tested on the CSM pin/ball-on-disk tribometer. Each test has duration of sixty minutes, surface speeds of 100 rpm, and load of 20 N.

In the analysis of this data, the best formulations give the lowest coefficient of friction (Figure 32 and Table 8). When analyzing the images of the wear scar, a smaller radius indicates better performance of the lubricant (Figures 33-35).

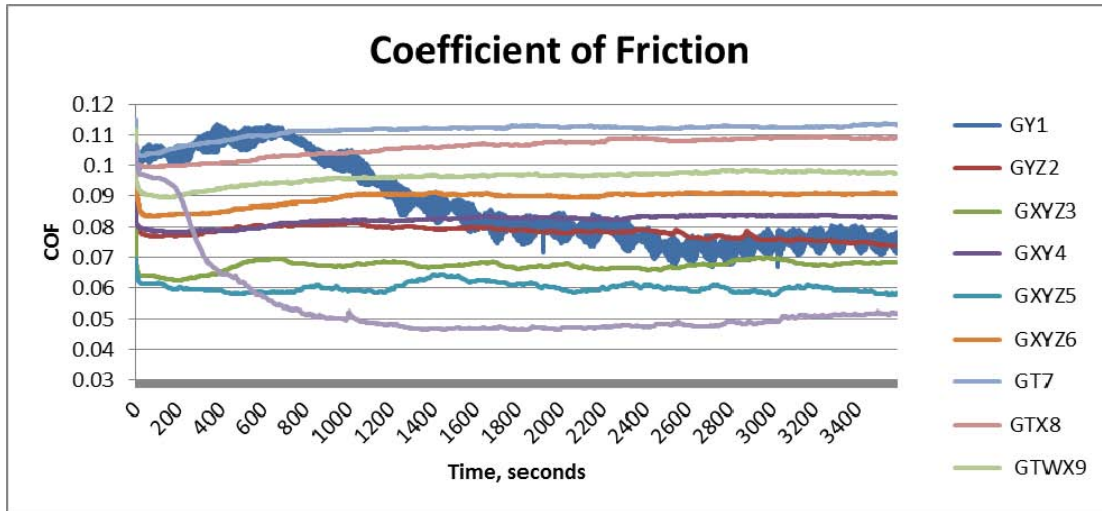


Figure 32. COF comparison for gear oil and modified nanolubricant formulations using Pin-on-Disk test

Table 8. Tribological performance of gear oil with modified formulations of nanolubricant using Pin-on-Disk Test

Samples	COF, μ	Wear Scar, μm
GY1	0.088	152.9
GYZ2	0.078	140.7
GXYZ3	0.067	153.6
GXY4	0.082	134.6
GXYZ5	0.060	153.0
GXYZ6	0.089	122.5
GT7	0.111	125.1
GTX8	0.106	143.5
GTWX9	0.096	106.6
GTYZ10	0.054	139.3

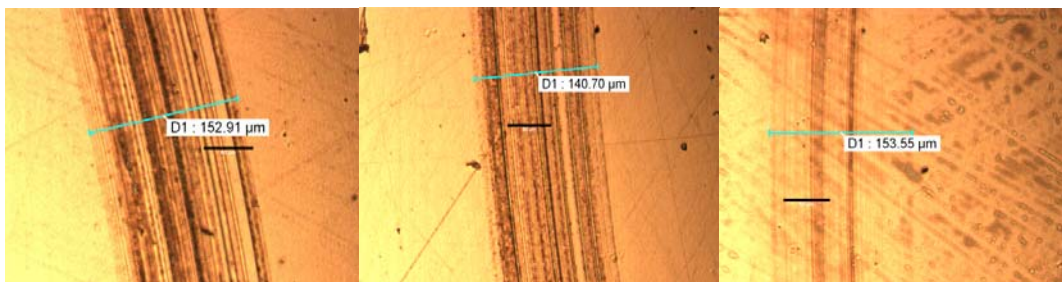


Figure 33. Optical microscope image with wear surface on disc for formulated gear oil with nanolubricant formulations (GY1, GYZ2, and GXYZ3)

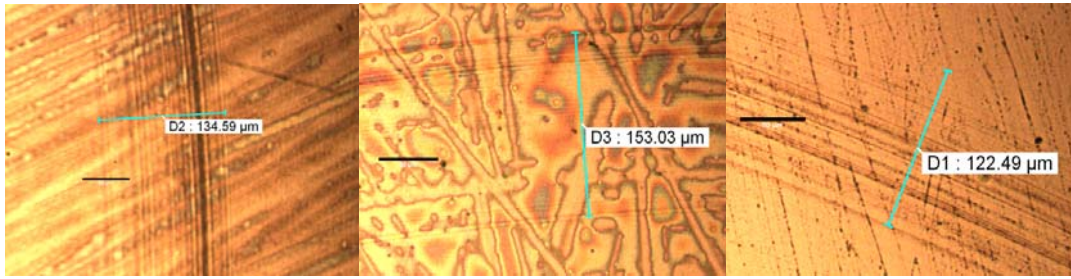


Figure 34. Optical microscope image with wear surface on disc for formulated gear oil with nanolubricant formulations (GXY4, GXYZ5, and GXYZ6)

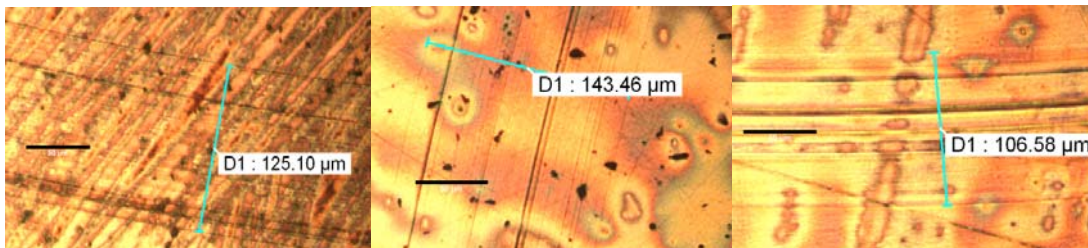


Figure 35. Optical microscope image with wear surface on disc for formulated gear oil with nanolubricant formulations (GT7, GTX8, and GTWX9)

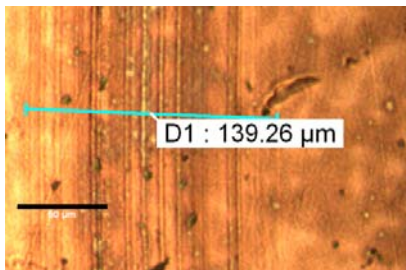


Figure 36. Optical microscope image with wear surface on disc for formulated gear oil with nanolubricant formulation (GTYZ10)

In the presented wear images for nanolubricant GT-based formulations (GT7, GTX8, GTWX9, and GTYZ10), the highest coefficient of friction corresponded to the smallest wear scar. Reasons for this might be a deeper wear scar than the picture can capture in two dimensions. Surface profilometry and wear volume measurements may give a better understanding of the lubrication and wear mechanisms for these formulations. The specimen tribofilms were analyzed using XPS, Auger, and TOF-SIMS and results will be presented in the next report.

Using the coefficient of friction rankings for the Pin-on-Disk tribotesting, the best additives were GT7 and GTYZ10. Performance for both of these additives corresponded

well to their particle size analysis (PSA) results and also gave fairly good results in the Block-on-Ring test.

In summary, the tribotesting results of gear oils with nanolubricant formulations should be considered ongoing, as more data is collected for chemical analysis of tribofilms using analytical techniques like XPS, Auger, and TOF-SIMS. More testing of the lubricant additives will be done using Pin-on-Disk, combined with Raman Spectroscopy and FZG testing in the fourth quarter. The results are encouraging, and further information developed in the next reporting period will undoubtedly provide even better understanding of the nanolubricant additive performance in gear oils.

4.2. Tribological performance of nanolubricant in greases

The following table summarizes the list of additives that were added to base grease (NLGI-2 EP Li-base grease with 5-10 weight % of zinc compounds) and tested for tribological performance using the 4 Ball test and EP 4 Ball Test.

Table 9. Grease samples for tribological testing using 4 Ball and EP 4 Ball Tests

Grease
Grease + μ -MoS ₂
Grease +n-WS ₂
Grease +nanolubricant 1 ZX
Grease +nanolubricant 2 WX

Four Ball Test (ASTM D2266)

The greases were tested for wear efficacy following the ASTM D 2266 standard with conditions of 40 kg load, 1200 rpm and 1 hour test duration.

As is observed from Figure 37, the base grease gave a wear scar diameter of 0.6mm. Adding MoS₂ (micron-sized particles) did little to improve the performance of the base grease. However, significant reduction in the wear scar diameters was observed when nanolubricant 1 ZX and nanolubricant 2 WX were added to the grease. Nanoparticles of

WS₂, on the other hand, showed antagonistic behavior, giving a wear scar diameter ~10% greater than that obtained with the base grease.

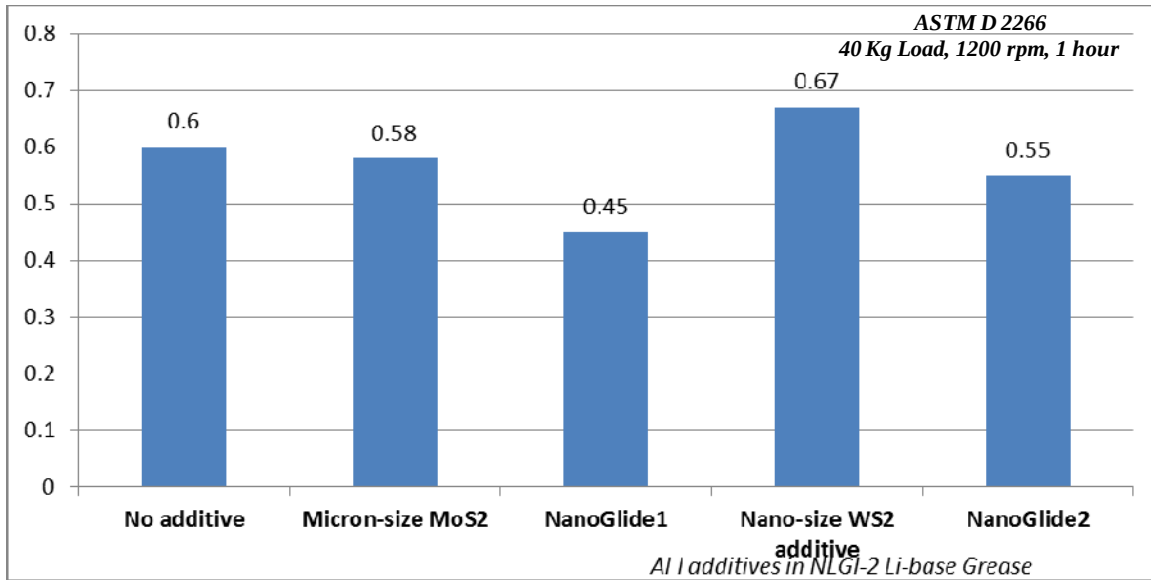


Figure 37. Wear scar diameter comparison for greases using 4 Ball test

EP Four Ball Test (ASTM D2596)

This method is used to determine the load-carrying properties of lubricating greases. Two key results are obtained with this method - Load Wear Index and Weld Load. The rotating speed of the spindle is 1770 +/- 60 rpm. Lubricating greases are brought to 27 +/- 8 °C and then subjected to a series of tests of 10 second durations at increasing loads until welding occurs.

Load wear index (LWI) is the measure of the relative ability of the lubricant to prevent wear under applied loads. As seen in Figure 42, nanolubricant 1 ZX shows the highest LWI indicating that the benefit of nanolubricant is realized.

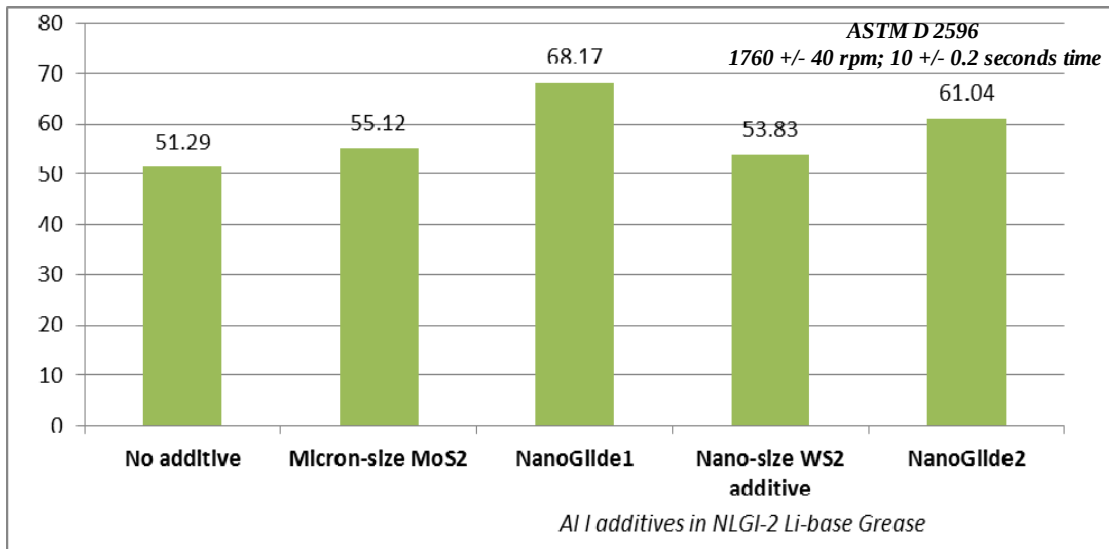


Figure 38. LWI comparison for greases using 4 Ball test

The Weld Point is the lowest applied load in kilograms at which the rotating ball in the Four Ball EP test either seizes and welds to the three stationary balls, or results in extreme scoring of the three balls. It is a measure of the extreme pressure properties of the lubricants.

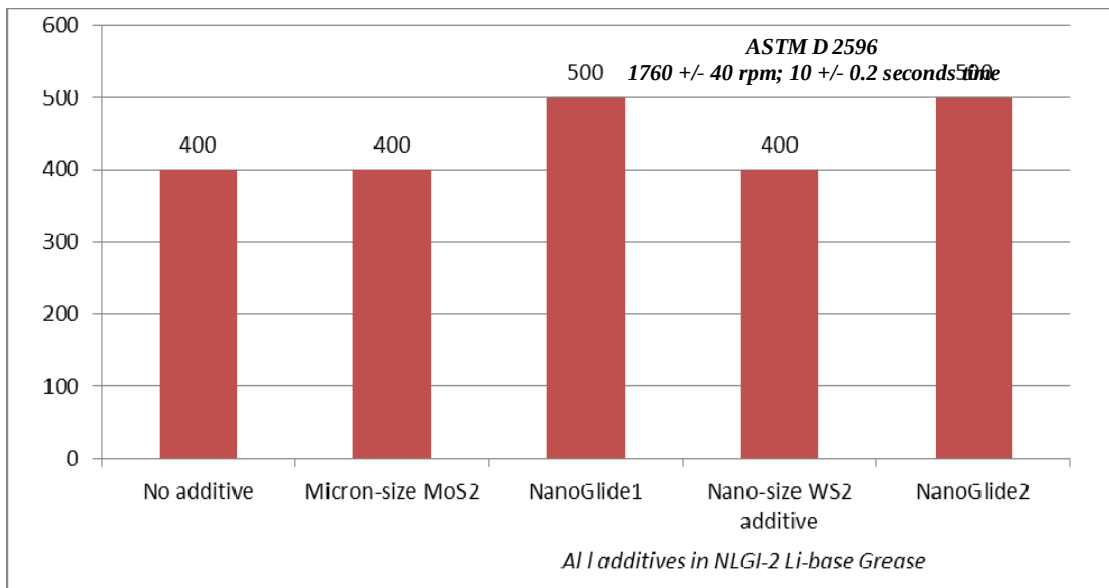


Figure 39. Weld point comparison for greases using 4 Ball test

All of the nanolubricant versions in grease gave better wear and LWI performance than neat grease, grease with WS₂ nanoparticles and grease with MoS₂ micron size

particles. Among all of the five greases tested, grease with nanolubricant 1 ZX proved to be the best with the lowest wear scar numbers and highest LWI and weld load.

4.3 Analysis and testing of structure-properties-application relationship (*University of Arkansas subcontract*)

The University of Arkansas is investigating the performance of nanolubricants when added into gear oils, using a Pin-on-Disk test and a test vehicle based on a real gearbox housing (FZG test).

Pin/Ball-on-Disk tribotesting

Gear oils (premium gear oil and non-premium oil with nanolubricant formulation) have been subjected to tribological studies and comparison. Testing has been performed on the CSM pin/ball-on-disk tribometer. The Stribeck curve was chosen as a method to compare the performance of the oils. To generate the curve, several test stages were performed using the same sample and wear track. Each stage had a duration of five minutes at the following decreasing surface speeds then back up again: 12 cm/s, 10 cm/s, 8 cm/s, 4 cm/s, 2 cm/s, 1 cm/s, 0.5 cm/s, 1 cm/s, 2 cm/s, 4 cm/s, 8 cm/s, 10 cm/s, and 12 cm/s.

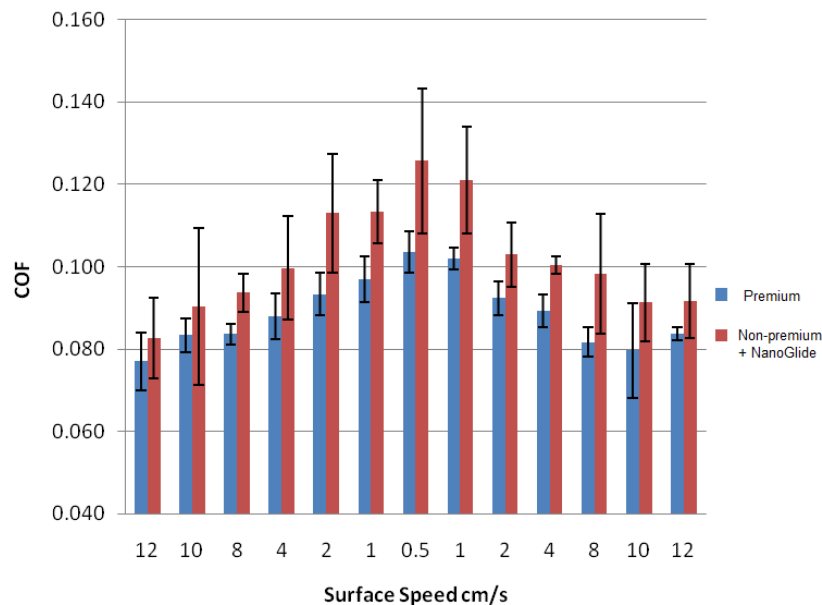


Figure 40. COF comparison of premium gear oil vs. non-premium gear oil with nanolubricant (initial formulation)

Figure 40 above, is based on three tests of both samples to show repeatability of the performance. For further comparison, the wear scar diameter of the ball was analyzed using a microscope. The results are shown in Figure 41.

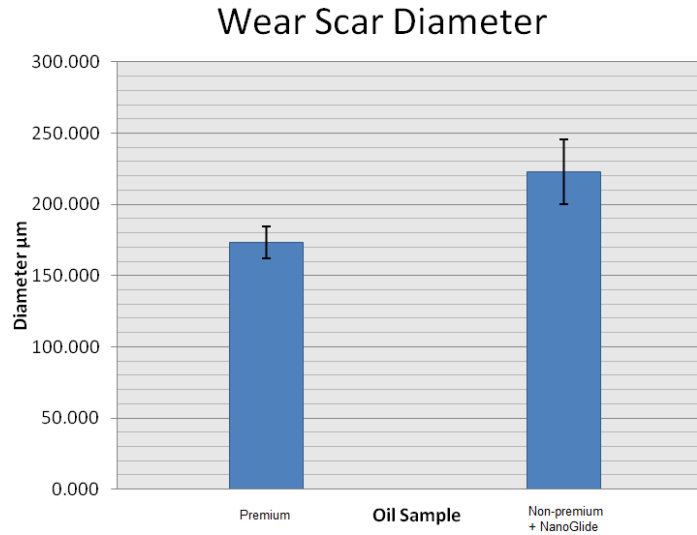


Figure 41. Wear scar diameter comparison of premium gear oil vs. non-premium gear oil with nanolubricant (initial formulation)

These results showed that the nanolubricant additive (initial formulation) in the non-premium oil did not outperform the premium gear oil. The new modified formulation of nanolubricant (described earlier in Task 3 of this report) will be used to improve the non-premium gear oil performance.

4.3. Design of gear testing set-up for the study of lubricant performance (project

subcontract, University of Arkansas)

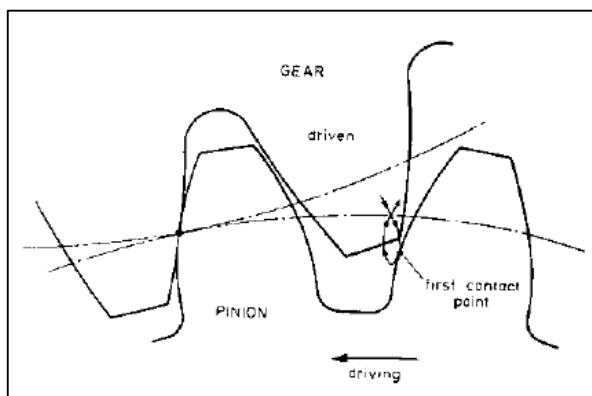


Figure 42. Gear meshing [4]

Gears like other mechanisms have specific lubrication needs due to their high point loading. This contact pressure is much higher than that experienced by crankshaft journals and piston cylinders in an engine; therefore higher weight oils are used.

Even with these high viscosity oils, at higher loads gears still undergo boundary lubrication. In this condition the pressure between the two surfaces is so high that the fluid is squeezed out of the way and the surfaces come in contact. This metal to metal contact increases the wear and friction, reducing the life of the part. For this reason solid particle additives can be used to avoid the surface to surface contact. The particles suspended in the oil will become deposited between the asperities of the surface and aid in lubrication.

The pin-on-disk and four ball tests only account for the sliding friction in the gear pairs. During tooth interface the surfaces in contact change angle while sliding occurs resulting in both a rolling and sliding friction mechanism during operation. This is illustrated in figure 1 above. Also, the gear tooth contact is a non-continuous process and both tests discussed above are continuous. Because of these differences there can be discrepancies in results from bench testing to real world performance.

For gear applications, the FZG test is the most effective large-scale test; the rig consists of a motor that drives two shafts through a slave gear box. One shaft has a torque measuring instrument and the other a loading clutch. These two shafts then input to the test gear box (Figure 42). The two standard tests for this rig are the scuffing test and the pitting test. The scuffing test uses profile A gear specimens and consists of incremental loading stages. The rpm is constant at 1400 rpm and run for 15 min at each stage with increasing load. When the wear scar on all teeth

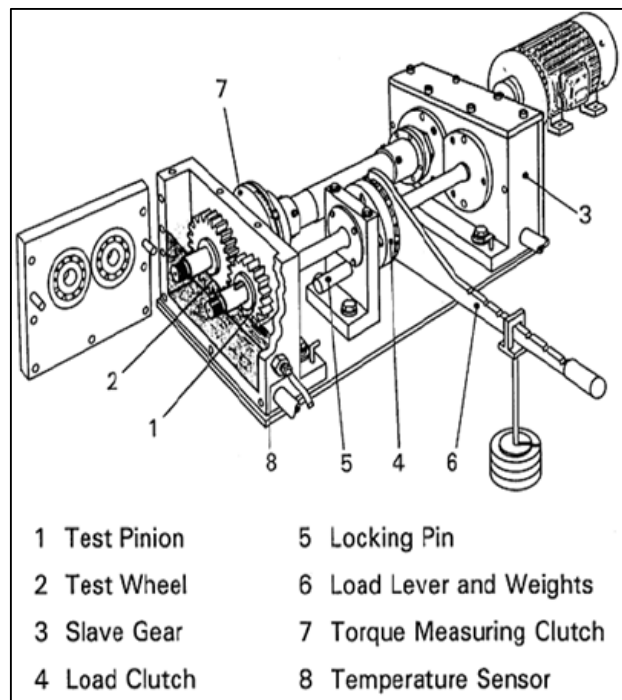


Figure 43. FZG test rig [4]

covers the tooth width the test is complete. The pitting test uses profile C gear specimens and is performed at a constant rpm and load until 4% of the tooth area is pitted [4].

The FZG rig can also be used to measure the differences in power loss for different gear oil formulations. One method is to perform several no-load runs at different speeds,

then several load runs at the same speeds. During those runs measurements of the motor torque and speed or electrical consumption of the motor can be taken to get the power loss comparison. The no-load runs will give the windage loss from the gears churning in the oil and the load runs will give the losses from the tooth interfaces.

Figure 44 shows the outline of the design described in this paragraph. A pulley system is used to convert the 1760 rpm of the motor to the required 1440 rpm of the test procedure. It is connected to the slave gears. Also, due to the tension of the pulleys this gearbox has a larger bending stress added to the shaft instead of mostly torsion stress. This increases the required shaft and bearing size for the gearbox. The gearbox is connected to the clutches using LoveJoy spider couplers to absorb any unwanted vibrations or slight misalignment. The system is mounted to a heavy cart for mobility but can be locked down during testing.

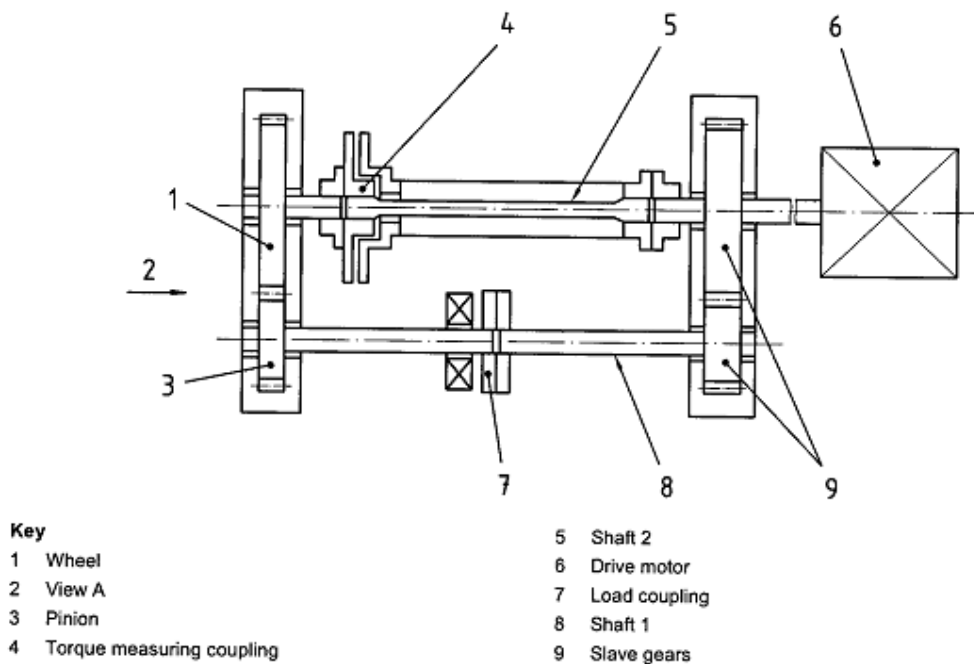


Figure 44. Schematic section of the FZG gear test machine [4]

Test bed configuration

For gear applications the FZG is a very effective large scale test; the rig consists of a motor that drives two shafts via a slave gear box. One shaft has a torque measuring instrument and the other a loading clutch. These two shafts then input to the test gear box.

The two main standards for this rig are the scuffing test and the pitting test. The scuffing test uses profile A gear specimens and consists of loading stages. The rpm is constant at 1450 rpm and run for 15 minutes on each stage with increasing load. When the wear scar on all teeth covers the tooth width the test is complete. The pitting test uses profile C gear specimens and is performed at constant rpm and load until 4% of the tooth area is pitted [5].

Test Features	
12 load stages	5 to 535 Nm
Constant speed	1450 rpm
Constant temp	90°C
Duration	21,700 rev/stage
Center Distance	91.5 mm
Test gear pitch	Mod. 4.5

Table 10. FZG test specifications [6]

the test oil is held at 90°C. Maintaining the oil temperature is important for two reasons; the first of which is to keep the viscosity of the oil the same between tests. Second and equally important is that the properties of steel changes with temperature, so by keeping the temperature the same the surface strength of the gear teeth is held constant. There are 12 load stages that range from 5 to 535 Nm on the pinion gear, each is ran for 21,700 cycles per load stage. The specifications of the test are shown above in table 10.

The standard also calls for a very specialized set of gears. The material element ratios and hardening characteristics are controlled; as well

The focus is on measuring the improvement in the load carrying capacity of the oil plus additive, so the test bed is being designed with ISO 14635-1 in mind. The speed of the motor driven shaft is maintained constant at 1450 rpm and the temperature of

Dimension	Symbol	Numerical value	Unit
Shaft centre distance	a	91,5	mm
Effective tooth width	b	20	mm
Working pitch diameter	pinion d_{w1}	73,2	mm
	wheel d_{w2}	109,8	mm
Tip diameter	pinion d_{a1}	88,77	mm
	wheel d_{a2}	112,5	mm
Module	m	4,5	mm
Number of teeth	pinion z_1	16	
	wheel z_2	24	
Profile-shift coefficient	pinion x_1	0,853 2	
	wheel x_2	-0,50	
Pressure angle	α	20	Degrees
Working pressure angle	α_w	22,5	Degrees
Pitch-diameter circumferential speed	v_w	8,3	m/s
Addendum engagement	pinion a_{a1}	14,7	mm
	wheel a_{a2}	3,3	mm
Sliding speed at tooth tip	pinion v_{gs1}	5,56	m/s
	wheel v_{gs2}	1,25	m/s
Specific sliding at tooth tip	pinion ζ_{E1}	0,86	
	wheel ζ_{A2}	0,34	
Specific sliding at tooth root	pinion ζ_{A1}	-0,52	
	wheel ζ_{E2}	-5,96	
Hertzian contact pressure	P_0	$14,7 \sqrt{F_{Ht}^*}$	N/mm ²

* F_{Ht} = normal tooth load in newtons (see Table 3).

Material	Case-hardening steel with restricted hardenability to 2/3 of the lower scatter band. Material composition: C = 0,13 % to 0,20 % Si = max. 0,40 % Mn = 1,00 % to 1,30 % P = max. 0,025 % S = 0,020 % to 0,035 % Cr = 0,80 % to 1,30 % Mo = max. 0,12 % Ni = max. 0,30 % Al = 0,02% to 0,05 % B = 0,001% to 0,003 % Cu = max. 0,30 %
Heat treatment	The test gears are carburized and case hardened. The case depth at a hardness of 550 HV10 shall be 0,6 mm to 0,9 mm. The surface hardness after tempering: 60 HRC to 62 HRC, core strength in tooth root centre: 1 000 N/mm ² to 1 250 N/mm ² (determined in accordance with ISO 4964 based on Brinell hardness). Retained austenite should be nominally 20 %.
Gear accuracy grade	Q5 according to ISO 1328-1
Arithmetic roughness of flanks R_a	R_a is separately determined for left and right flanks, measured each at three flanks per gear across the centre of the tooth parallel to the pitch line; measuring parameters according to ISO 4287: measured length $l_t = 4,8$ mm, cut-off length $l_c = 0,8$ mm; velocity = 0,5 mm/s; using a skid. Average roughness (relating to manufacture batches of a minimum of a 100 gear sets) Pinion: $R_a = 0,35 \mu\text{m} \pm 0,1 \mu\text{m}$ Gear: $R_a = 0,30 \mu\text{m} \pm 0,1 \mu\text{m}$ Maximum roughness (average of three measurements according to the described method and valid for 95 of 100 tested gears). Pinion and gear: $R_a = 0,5 \mu\text{m}$
Grinding	Maag criss-cross grinding (15° method), 154 r/min of generating stroke drive
Flank modification	None

Table 11. Test gear specifications [6]

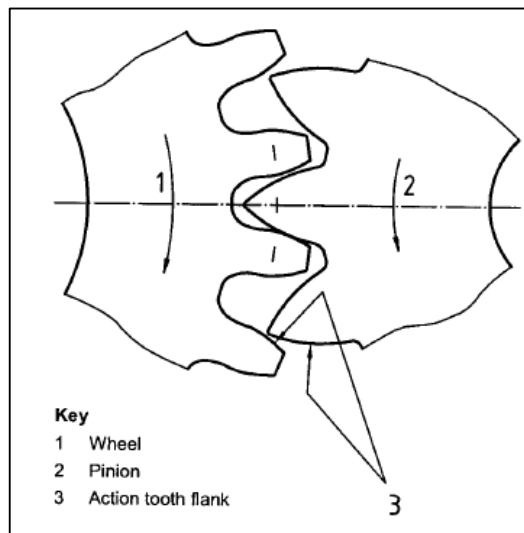


Figure 45. Test gear profile shift [6]

as, the roughness of the gear tooth surfaces. Detailed characteristics can be found in table 11. The gears are an odd pitch of module 4.5 that is not available off the shelf and the test specifies that they have a center distance of 91.5 mm. Given that the specified gear ratio is 1.5, the center distance is slightly greater than normal design parameters for this gear set. This difference must be accounted for in the design of the slave gear box. Furthermore, the profile of the gear teeth is shifted in order to obtain a controlled lubrication regime. This shift is illustrated in figure 49. During testing

the ground surfaces of the gear teeth will begin to scuff at the center and which ever loadstage causes the scuffing to extend the full width of the gear is the load carrying capacity of that oil. For oils up to GL-5 classification the test gears used have a face width of 20 mm and for extreme presure (EP) oils a 10 mm face width is used. This is because EP oils reach load stage 12 of the 20 mm gears without failing thus the face width of the gear is reduced to increace the surface pressure.

The standard layout for the FZG test rig is illustrated in figure 48. The design incorporates a power loop in which the drive motor only has to overcome the friction in the system. The load is applied by adding an angle of twist to the pinion shaft before starting the test. This preloads the gears so they can experience up to 395 ft lbs of torque during testing with only a 7.5 hp motor. To accomplish preload the pinion shaft is spliced in the middle connected by a flange style coupler. The coupler is loosened and one side is locked in place while the other side is torqued. Once proper torque is achieved the flange is tightened and then unlocked. This step is repeated for every load stage. The other shaft uses a slip clutch in order to ensure that the gears are not over torqued during the test.

The FZG rig can also be used to measure the power loss of the gear oil. One method is to perform several no load runs at different speeds, then several load runs at the same previous speeds. During those runs measurements of the motor torque and speed or electrical consumption of the motor is taken to get the power comparison. The no load runs

will give the windage loss from the gears churning in the oil and the load runs will give the losses from the tooth interfaces.

As can be seen in figure 46, the efficiency measurement is taken farther. Each shaft is equipped with a strain gauge to measure the torque experienced by the gears. The strain gauges are wired to a slip ring that allows the signal to be transmitted from the rotating shaft to the data acquisition system (DAQ). This way instead of measuring overall power consumption, one can measure the torque loss between the gears due to friction. Also, the strain gauges could be used to measure the variation in torque to determine when a tooth has failed during a pitting test. In addition to torque monitoring the gear box temperature can be plotted via DAQ to determine how much heat is generated from friction in the gear set to compare different oils.

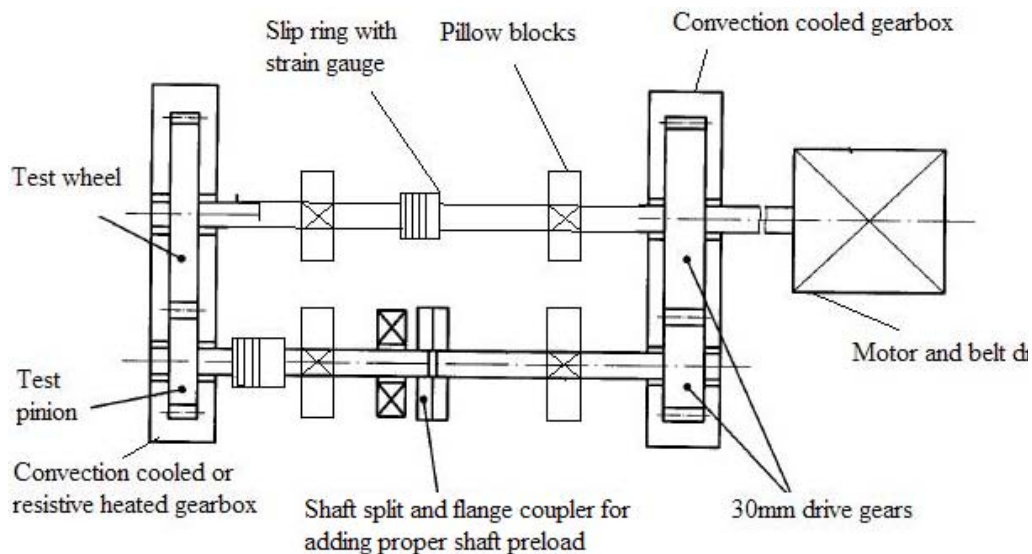


Figure 46. Modified FZG layout

Due to the controlled nature of the manufacturing of these test gears they are highly expensive. If purchased directly from the manufacturer Strama in medium quantities the 20 mm width gear pair will cost approximately \$1,000.00 and the 10 mm will run about \$1,200.00. Thus a viable alternative is necessary for preliminary testing and prove out. For this purpose a set of gears from Quality Transmission Components has been chosen. They are off the shelf gears that are readily available and they fit the center distance requirement of the machine. The gear set is low cost at about \$200.00 and the details are listed below in table 12. These gears would of course not replace the standardized gears, but repeatability could be analyzed to see if they can make a viable comparison between oils. The alternate

	Pinion KSSA3-24	Wheel KSSA3-36
Number of Teeth	24	36
Design	Metric	Metric
Pressure Angle	20°	20°
Gear Center	Center Bore	Center Bore
Metric Gear Dimensions		
Module	Mod 3	Mod 3
PD	72.00 mm	108 mm
OD	78.00 mm	114 mm
Face Width	30.00 mm	30.00 mm
Overall Width	30.00 mm	30.00 mm
Bore Diameter	15.00 mm	20.00 mm
Material	Hardened	Hardened
Mounting	Hubless; Simple Bore	Hubless; Simple Bore

Table 12. Alternate test gears [7]

The current progress of the 3D FZG model is shown in figure 47. As one can see the motor is connected to the slave gear box via a pulley system. Currently the gear box designs are completed and the means of connecting the two is underway. The pillow blocks for the connecting shafts are in place and an extra pillow block is added where the load coupling will be placed. This addition will insure that the shafts will not be bent while shaft pre-torque is applied manually. The gearbox is coupled to the intermediate shafts via LoveJoy spider couplers to absorb any unwanted vibrations and slight misalignment. The system is mounted to a heavy cart for mobility, but can be locked down during testing.

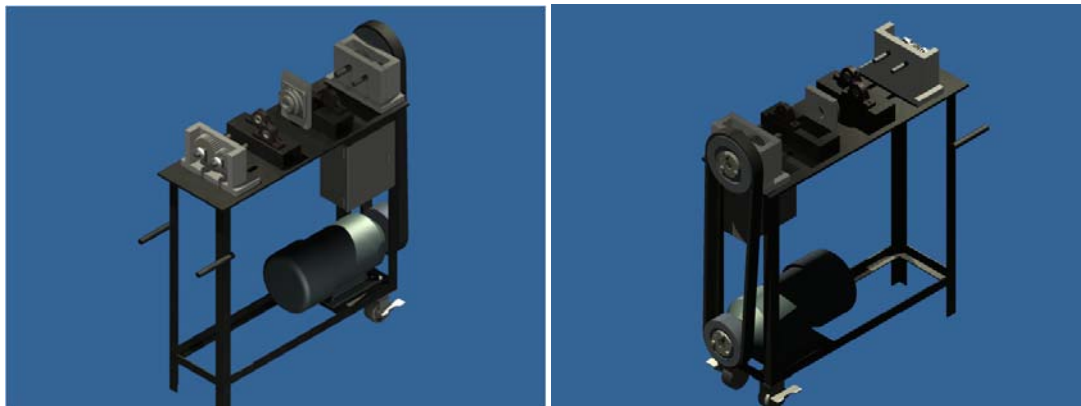


Figure 47. FZG model

The design for the pulley system has been completed for transmitting the required power and torque. The proper gear set has also been sized to insure life expectancy of the

test gears have a roughness as seen in real world applications as opposed to the extra finishing of the standardized gears. If repeatability can be maintained this aspect would be important to see if the nano particles become lost in the asperities of the rougher real world surfaces as opposed to the polished lab specimens. Though data from load carrying capacity is questionable until it can be analyzed, these gears would be completely viable for testing of efficiency between gears oils.

test rig. The shaft design and bearing layout have been completed and sizing of the system for the required life span is in progress.

Future work

The design process will continue with the load coupling that will entail a modified flange coupler that can be locked in place unbolted and then indexed to accomplish the twist in the connecting shaft need for the desired torque stage. From there the locations of the strain gauges will be determined and then the shaft will be sized in that location to allow enough yielding for the strain gauge to function properly. Once the test bed model is completed a full drawing package will be made up for machining and future maintenance. Overall the progress is well underway and assembly will be delivered by June 17, 2011. Testing should commence once the machine is proved out and calibration is satisfactory.

4.4. Effects of nanolubricants addition into regular military gear oil and their tribological performance using WAM test (testing at Wedeven Associates)

Although the problem of gearbox failure is complex, some of the past efforts tried to focus on one solution at a time, for example lubrication and the lubricant. While progress has been made, the problem still remains. Since tribological systems and failures are often multi-dimensional involving several variables and parameters; a systematic approach that takes into account all the relevant lubrication mechanisms is needed. The approach proposed in this section, ties the lubrication mechanisms to the various failure mechanisms using unique systematic test methodologies. This approach facilitates a highly efficient and cost-effective means of evaluating advanced additive concepts and other potential technologies to address wind turbine gearbox reliability issues. The development and scale-up of nanostructure additives to be evaluated with large full-scale testing will be cost prohibitive. On the other hand, simple laboratory bench-top tests such as pin-on-disc or twin-roller tests only provides fundamental behavior and do not capture all the relevant lubrication mechanisms in gears and bearings. Consequently, such test results seldom correlate with observations and results from field or from full-scale testing. Even the current gear test method being developed by the wind turbine industry for lubricant qualification is problematic. This is due to gear material and fabrication inconsistencies and complex gear meshing conditions which cannot be isolated for the controlling lubrication and failure mechanisms. The foundation of the proposed methodology in this work is the

connection of laboratory screening test with observed field and full-scale testing results and observations – a change from current practices.

This innovative approach has been successfully used by Wedeven Associates, Inc. in development of advanced gear and bearing materials and lubricants for aeropropulsion systems. The Systematic Tribology approach, with U.S. Air Force and Navy support, provided a community of action that resulted in the development of an advanced stainless bearing/gear material Pyrowear 675, along with compatible oil additive technology. WAM testing methods for scuffing, wear, and micro-pitting were used for all the tribology development and qualification testing. The technology is now being introduced into military, commercial engine, and gearbox systems. This efficient and successful specialized approach is to be utilized in the scale-up and validation of NanoMech nanostructure additives for wind turbine gearbox applications.

This task is designed to evaluate nanolubricant additive formulations with two types of tests. One proven test method for fundamental evaluation of lubricant additive formulations affecting wear and scuffing is a test method used for qualification of jet engine oils for both military and commercial engines. The High Speed Load Capacity Test Method, or a modified version of this test method, shall be used to evaluate laboratory and production samples of nanostructure additive formulations. The test method is illustrated in Figure 48.

The test method in Figure 48 runs through progressively more severe contact conditions from near full-film EHD lubrication to mixed-film lubrication, boundary lubrication, wear and scuffing. The test conditions are selected to represent a contacting point on a gear tooth mesh where the contact conditions are most vulnerable to scuffing damage. Traction (friction) behavior reflects asperity wear and the robustness of the material and oil formulation is judged by scuffing. This test method has already been successfully used to evaluate laboratory grade nanolubricant formulations.

The outcome of these tests shall provide opportunity for enhanced nanolubricant formulations and to assure laboratory and production-scale materials are successfully and repeatedly produced in scaled up production pilot plant.

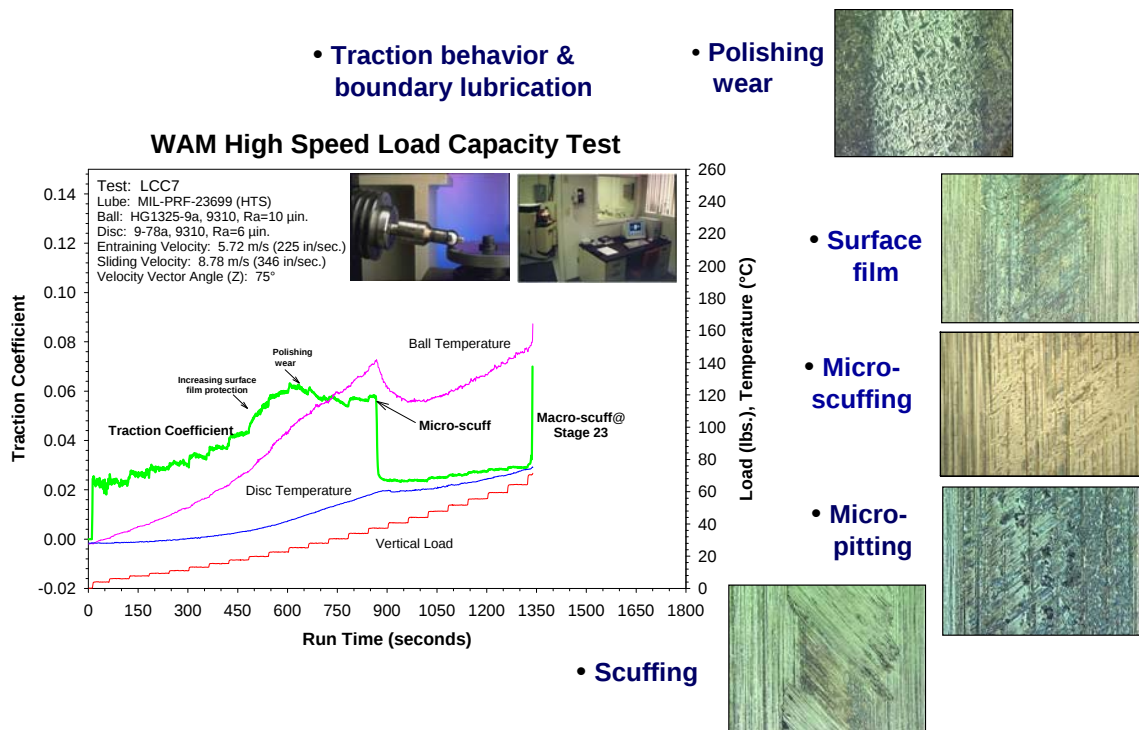


Figure 48. High Speed Load Capacity Test Method

The WAM High Speed Load Capacity Test Method provides traction and scuffing evaluation of oils with independent control of entraining and sliding velocities, which are defined as below:

$$U_e = \frac{1}{2} (U_b + U_d)$$

$$U_s = (U_b - U_d)$$

Where, U_b = surface velocity vector of the ball at the contact point

U_d = surface velocity vector of the disk at the contact point

The test conditions have been modified for high-load carrying oils and are shown as below:

	Standard protocol	Modified protocol
Angle	75°	95°
U_e	225 in/sec	158 in/sec
U_s	346 in/sec	346 in/sec

Micro-scuffing is associated with surface damage at low load stages whereas macro-scuffing is associated with complete loss of surface integrity. The measurements of traction coefficient identify events like scuffing and micro-scuffing and they also reflect the continual interactive process between oil chemistry and mating material pair within the contact.

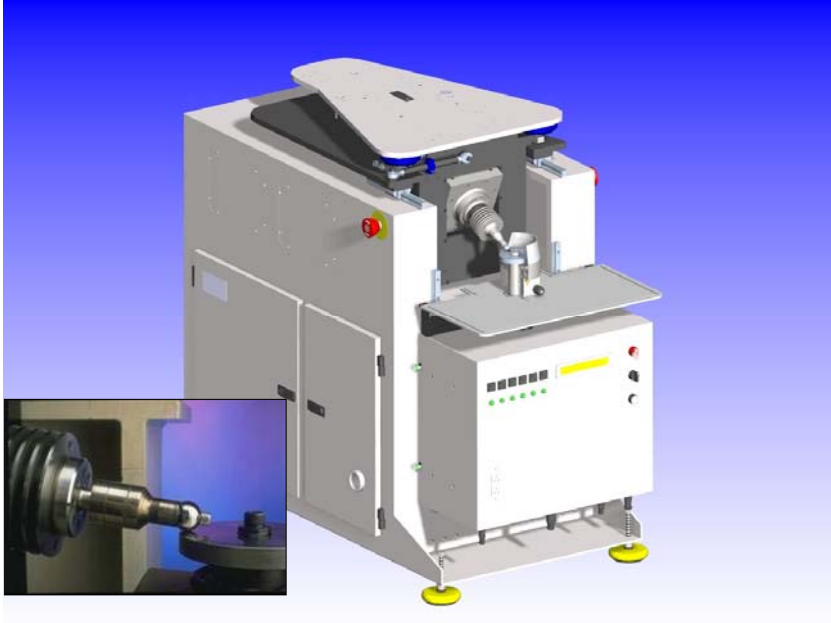


Figure 49. WAM test machine

Scuffing load capacity tests were conducted with a nanolubricant additive version formulated in two qualified aviation oils, ExxonMobil Jet Oil II and AIR BP Turbo Oil 25. The former oil is a STD MIL-PRF-23699 jet engine oil and the later oil is a DOD-PRF-85734 aviation gearbox oil. The results show little difference in scuffing performance. There were subtle differences in traction (friction) coefficient behavior. This is attributed to the presence of the nanoparticles and its effect on polishing wear.

ExxonMobil Jet Oil II was re-formulated with 2% L1NG1D3XYZ and AIR BP Turbo Oil 25 was re-formulated with nanolubricant 2% L1NG1D2WX. The average scuffing stage of the BPTO 25 formulation was boosted from 20 to 23 with the second formulation. BPTO 25 was then re-formulated again with nanolubricant 2KDS16-1.

WAM High Speed Load Capacity Test Method

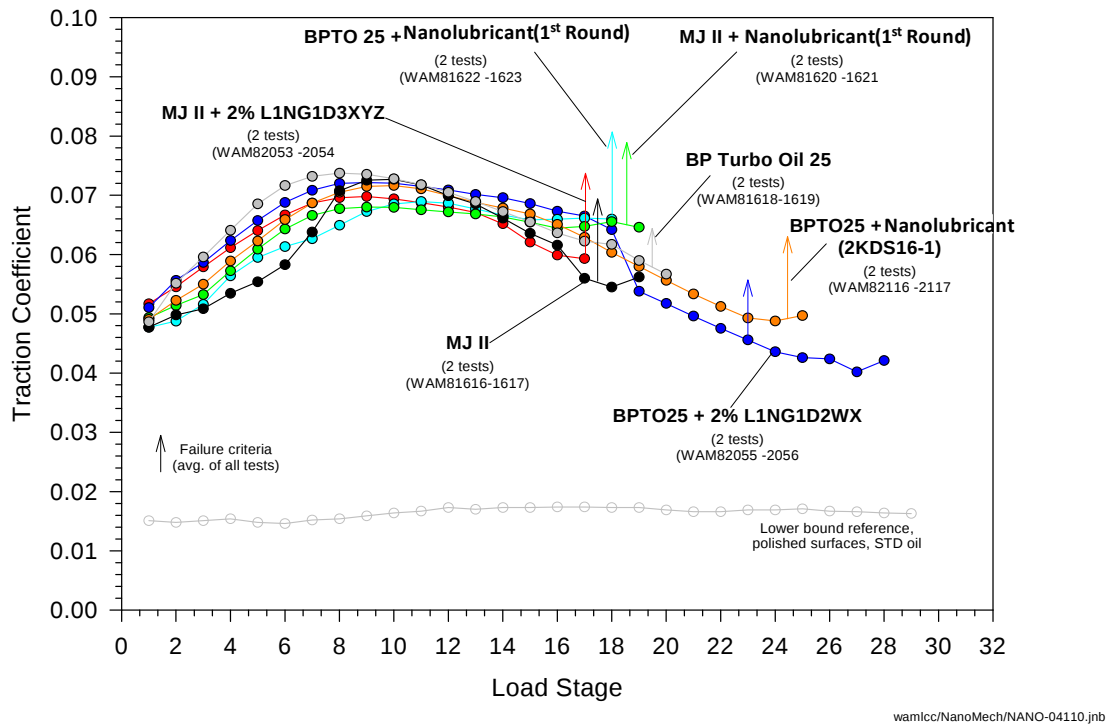
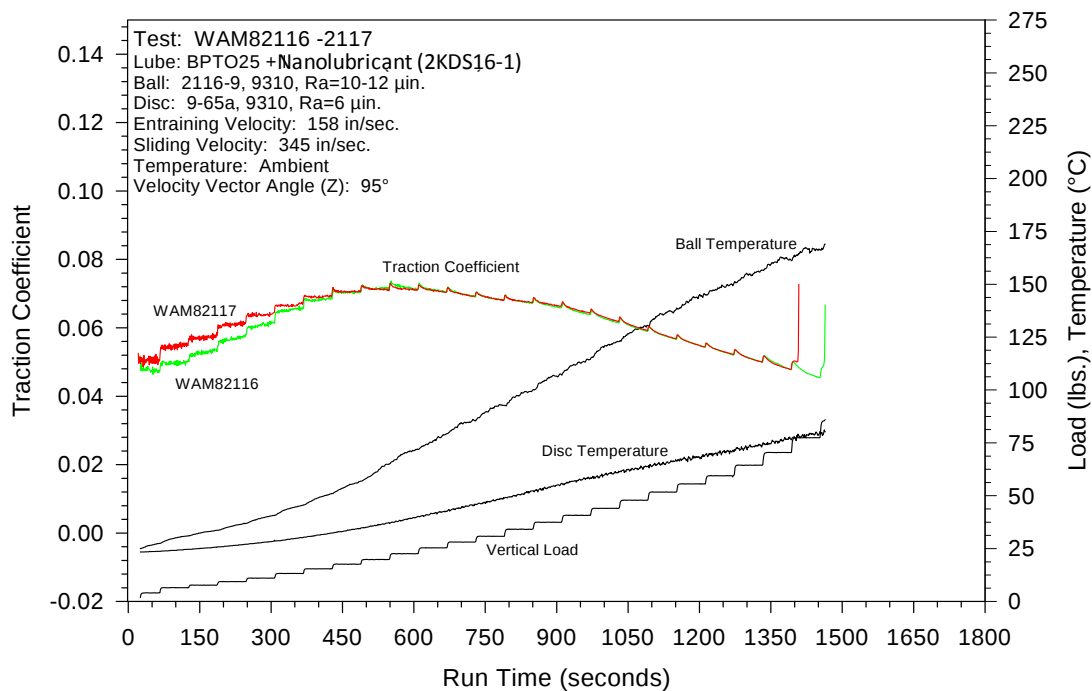


Figure 50. WAM testing of nanolubricant in BPTO 25 and MJ II oils

1. Air BP BPTO 25 formulation with 2KDS16-1 results in an average scuffing stage of 24.5, compared to failure stage of 19.5 with the unformulated oil and both formulations show different traction (wear) behavior. The rate of rise in traction coefficient with the load stage was observed to be higher in the BP BPTO 25 Oil indicating a resistance to polishing action of roughness features. However, the surface film chemistry that provides early resistance to polishing wear is not sufficient to prevent early scuffing and thus a failure stage of 19.5 is observed with the unformulated BPTO 25 oil. The high scuffing failure stage for BPTO 25 with 2KDS16-1 without a micro-scuffing event is indicative of the highly responsive chemical film forming capability of nanolubricant from wear and scuffing and attributed to the load carrying additive package nanolubricant.

2. The traction coefficient behavior and scuffing load stage is repeatable.

WAM High Speed Load Capacity Test Method



wamcc/NanoTech(NANO-04110a.jnb)

Figure 51: WAM test results for two different runs of the same sample 2KDS16-1

As can be observed from the Figure 51, two tests of each formulation were conducted for ensuring repeatability in traction coefficient and failure load stages. WAM 82116 and 82117 are two tests that were performed under the same test conditions using the same oil formulations (BPTO 25 with 2KDS16-1). The trend in the traction coefficient is observed to be similar with an observed average scuffing failure stage at 24.5. The macro stages were seen at 25 and 24 load stages for WAM 82116 and WAM 82117 tests, respectively. In both tests, no micro-scuffing event was observed.

3. The BPTO formulation with 2KDS16-1 does not encounter a micro-scuff or rapid wear event like the previous formulation with 2% L1NG1D2WX.

Micro-scuffing is generally associated with surface damage at low load stages where contact stresses are too low to cause “macro” scuffing. When traction is measured, micro-scuffing is generally detected by a rapid decrease in traction coefficient and the decline is associated with the removal of surface roughness features by plastic flow and rapid polishing wear. Additional purification methods were employed when formulating the BPTO 25 with 2KDS16-1 and thus lethal abrasive impurities that could have potentially been incorporated in the formulation during synthesis were removed. The presence of such impurities in the BPTO 25 formulation with 2% L1NG1D2WX could have been responsible for the occurrence of a micro-scuffing event.

4. A summary of the BPTO 25 formulations is given below:

BPTO 25 (Specification: DOD-PRF-85734, aircraft gearbox oil) demonstrates a scuffing failure load stage of 19.5 with a high traction coefficient that is attributed to the activation of anti-wear and extreme pressure chemistries in BPTO 25. This is a typical behavior observed in BPTO 25 oil.

Table 13. WAM High Speed Load Test

Oil Sample	Load Stages
BPTO 25	19.5
BPTO 25 +Nanolubricant Prescreening (1 st round)	17.0
BPTO 25 + 2%Nanolubricant L1NG1D2WX	23
BPTO 25 + 2%Nanolubricant 2KDS16-1	24.5

In the first round of WAM testing for BPTO 25 with nanolubricant (for pre-screening), a traction behavior different from that of BPTO 25 oil is observed, indicating a difference in wear behavior with nanolubricant. Lower load stage with nanolubricant is postulated to the nanolubricant chemistries that may be competing with the anti-wear and extreme pressure additives in the reference BPTO 25 oil.

To boost the performance of the BPTO 25 oil, different nanolubricant chemistry (L1NG1D2WX) was synthesized. Higher scuffing failure load stage was observed with this formulation. However, a micro-scuffing event was observed at load stage 18 indicating rapid removal of surface topographical features and rapid polishing wear. In order to overcome this shortcoming in the formulation, nanolubricant was re-formulated with 2% 2KDS16-1 in the BPTO 25 oil and the average scuffing failure load stage was observed to be 24.5 with no micro-scuffing event compared to failure load stage of 19.5 in BPTO 25 oil.

Accomplished Deliverables

1. Design of experiments for tribological testing;
2. Tribological testing of nanolubricant samples in motor oils using 4 ball test, EP 4 ball test;
3. Tribological testing of nanolubricant samples in military oils using WAM test;
4. Design of FZG gear test machine;
5. Tribological testing of nanolubricant samples in motor and engine oils using pin/ball-on-disc, and engine oil using 4 ball test and EP 4 ball test;

6. Investigating the effects of nanolubricants addition into regular military gear oil and their tribological performance using WAM test.

Conclusions

Discovery and invention-based nanolubricants address the diverse application needs of the Navy, including lower coefficient of friction, smaller wear scar, high loading capability, good strength of tribofilm and equally important, little or no time to respond to “dry and harsh” conditions and deliver a tribofilm as a result of plastic deformation, when trapped among asperities. Target applications expected to be of interest to the Navy, for on- and off- shore purposes, are bearings, gear boxes, and engines.

In the third quarter of this project, the initial two formulations of nanolubricant were modified to specifically address their application as additives in gear oils and greases. These improved formulations were investigated using chemical, structural, and tribological analysis. A Design of Experiments (DoE) approach for synthesis and optimization using a scaled-up production process was applied to analyze interactions among process parameters and to select optimal synthesis parameters to be used with optimal process time.

Tribological testing of nanolubricant additives in gear oils using Pin-on-Disk test and Block-on-Ring test, and in greases using 4 Ball test and EP 4 Ball test was performed, and evolution and comparison of their performance is presented and discussed in this report. The FZG gear test rig is being prepared and is on schedule.

This project has revealed several advantages of having nanolubricant in lubricant formulations (gear oils and greases). It provides advanced lubrication for severe friction conditions (extreme pressure and loads) by extending component life and lube-drain intervals in comparison to base oils and greases. It is a technology that could increase the efficiency and durability of machinery components, particularly gears, leading to longer operation intervals and lower maintenance costs. Another beneficial feature is that it is non-disruptive and insertable into current lubricant production processes, and there is a wide range of industrial applications in which it can be put to use.

The scaled-up process was developed and process parameters were optimized. Morphological and tribological properties of samples from the scaled-up production were compared with properties of samples from laboratory-scale production. The outcomes of this comparison show similar particle size distribution and level of agglomeration of

nanoparticles for both processes and shortened process time for the scaled-up process, thus contributing to the technical objective of extended shelf life and suspension stability of nanoparticle additives, and the commercial goal of increasing yield per batch with significant reduction in processing time.

The lubrication testing of modified formulations of nanolubricant in military oils was completed using the WAM test and gear testing set up (FZG test) was developed.

Future Work and Directions

1. Tribological testing of nanolubricant additives using a test vehicle based on real gearbox housing (FZG test) [NanoMech/University of Arkansas];
2. Cooperation with Navy Research Laboratory (NRL, Dr. Kathy Wahl) for studying *in situ* friction and wear behavior [NanoMech/NRL];
3. Understanding of nanolubricant behavior at the nanoscale loading contact using Raman *In situ* Spectroscopy of tribofilm formation [NanoMech/NRL/University of Arkansas].

Complementary analytical techniques will be used to fundamentally understand behavior of the nanolubricant's unique chemistries in tribofilms. The investigation of nanolubricant behavior will involve chemical and structural analysis (XPS, SEM, and TEM) for understanding tribological behavior in Pin/Ball-on-Disk. The University of Arkansas is exploring an active partnership with a leading Tribology group at the Naval Research Laboratory (NRL). The University of Arkansas will collaborate, through exchange of student, with Dr. Kathryn J. Wahl (NRL) in using a specially designed instrument at NRL for *in situ* friction and wear analysis. This tribology approach will provide a more detailed fundamental understanding of the behavior of the nanolubricant at the nanoscale, directly at the point of loading contact, showing plastic behavior of the nanoparticles using an optically transparent pin/ball. A Raman signal tapped through the optically transparent pin/ball will carry the chemical signature of the event as it is occurring. This will give first-hand insight into the fundamental mechanism for behavior of the above novel chemistries.

Cost and financial status

	Budget	Actual First Quarter	Actual Second Quarter	Actual Third Quarter as of 7/31	Actual Fourth Quarter and 6 months extension	Total
NanoMech, Inc.	\$707,727	\$77,374	\$110,288	\$307,874	\$186,895	\$682,431
University of Arkansas (subcontract)	\$61,261	\$0	\$0	\$34,034	\$27,227	\$61,261
Total costs	\$768,988	\$77,374	\$110,288	\$341,908	\$214,122	\$743,692

References

1. Malshe, A., Verma, A. (January 2006), Nanoparticles Based Lubricants, Patent Pending.
2. Malshe, A., Verma, A. (July 2006), Active Nanoparticles: Synthesis, Behavior And Applications, Patent Pending.
3. Komvopoulos, K., Pernama, S.A.; Ma, J.; Yamaguchi, E.S.; Ryason, P.R. (2005), Synergistic Effects of Boron-, Sulfur-, And Phosphorus-Containing Lubricants in Boundary Lubrication of Steel Surfaces Tribology Transactions, 48 (2), 218.
4. ISO 14635-1, FZG test method A/8,3/90 for relative scuffing load carrying capacity of oils.
5. - Hoehn, B., Michaelis, K., and Doleschel, A., 2001, "Limitations of bench testing for gear lubricants," Bench Testing of Industrial Fluid Lubrication and Wear Properties used in Machinery Applications, June 26, 2000 - June 27, Anonymous American Society for Testing and Materials, Seattle, WA, United states, pp. 15-32.
6. Bernd-Robert Hoehn, "Test Methods for Gear Lubricant".
7. ISO 14635-1, FZG test method A/8,3/90 for relative scuffing load carrying capacity of oils.
8. Quality Transmission Components (www.qtcgears.com)
9. Budynas, Richard and Nisbett, Keith, 2008, "Shigley's Mechanical Engineering Design" 8th edition, McGraw Hill.

Publications and presentations:

1. Article entitled "Advanced Nanolubricant Additives" was submitted to Compoundings Magazine of the Independent Lubricant Manufacturers Association (ILMA), 2010;
2. Presentation titled "Advanced Nanolubricant Additives for Formulated Oils" by Dr. Dmytro Demydov, Arunya Suresh, and Dr. Ajay P. Malshe, NanoMech at the Society of Tribologists and Lubrication Engineers STLE 65th Annual Meeting and Exhibition (Las Vegas, NV), May 2010;

3. Presentation titled “Active Nanoparticles-Based Novel Lubricant Additives to Improve Energy Efficiency and Durability” by Dr. Dmytro Demydov, Arunya Suresh, and Dr. Ajay P. Malshe, NanoMech at the STLE 66th Annual Meeting and Exhibition (Atlanta, GA), May 2011;
4. Presentation titled “Advanced multi-component Lubricant Additive in Lubricating Greases” by Arunya Suresh, Dr. Dmytro Demydov, and Dr. Ajay P. Malshe, NanoMech at the STLE 66th Annual Meeting and Exhibition (Atlanta, GA), May 2011.

5. Appendix A: Project Plan Timeline

Table A1. Technical Tasks

	Tasks	MONTH 1-2	MONTH 3-4	MONTH 5-6	MONTH 7-8	MONTH 9-10	MONTH 11-12
1.	<i>Designing of application-specific active nanolubricant</i>						
2.	<i>Synthesis, de-agglomeration and optimization of nanolubricant</i>						
3.	<i>Structural, chemical, and physical analysis of nanolubricant</i>						
4.	<i>Tribological testing of nanolubricant</i>						