RECENT IMPROVEMENTS IN THE VARIOUS PROPERTIES OF LITHIUM GREASES BY USING ADVANCES IN NANOTECHNOLOGY

Anyone who has changed a pillow block in the middle of a heat wave understands how much of a pain equipment maintenance truly is. This inconvenience raises the question; Can the interval between equipment maintenance be extended, and if so, how? The answer to this question is yes. By utilizing nanotechnology, grease life is extended, reducing the wear on the pillow block, and extending its life span. Nanotechnology is defined as the science, engineering and technology conducted at the nanoscale, or approximately 1 to 100 nanometers [1]. The application of nanoparticle additives in greases enhances these products and allows them to achieve longer operation, extended period between equipment maintenance, and improved fuel efficiency [2]. These upgrades will be increasingly sought after as the shift to electric vehicles (EVs) ramps up following California's ban on the sale of new gas-powered vehicles after 2035 [3]. As the demand for electric vehicles grows, so does the need for proper lubrication for these vehicles, often forcing companies to put research into both the improvement of the quality of their product and the minimization of their cost. This ideal product can often be produced with the use of nanotechnology.

Lubrication is used in any system that contains two surfaces that are in contact. ranging from a chainsaw all the way up to a nuclear reactor [4]. One of the more popular lubricants is grease, a semi-solid substance that reduces the friction between two surfaces and effectively decreases the temperature at that contact area. As with any product, there are certain areas where grease thrives and others where it needs improvement. This work reviews the areas in which grease (in particular lithium based greases) can have their properties enhanced with the use of nanotechnology and it also reviews some of the other current improvements being made in enhancing properties for greases in general.

Electric vehicles (EVs) require not only longer battery life, but also improved lubricating ability. Lithium greases are soap based, semi-solid lubricants produced by the saponification of lithium hydroxide, or in some cases lithium carbonate [5]. These greases are in high demand, as their high dropping point temperatures, increased adherence to metal, resistance to moisture, as well as being noncorrosive, make them very desirable [5]. Like every other consumable good, companies and their researchers are looking for additional ways to improve both the efficiency and excellence of this product. This stems from lithium's recently shown volatility in price, beginning in 2016 and continuing to present day [5]. After setting aggressive goals for EV production, the Tesla company sent the price of lithium to the moon, making its purchase almost impossible for price conscious markets such as India [5]. This volatility showed companies that this expensive element was not to be wasted and improved efficiency was a financial necessity.

This need for improved performance facilitated the investigation of utilizing carbon base nano-additives in lithium greases. This research, completed by Sadeghalvaad et al., aimed to examine the effects carbon dot (C-dot) nanoparticles had on lithium grease [6]. Upon synthesizing these nanoparticles to the lithium-based grease, different weight percentages were tested (0.1,0.2,0.4,0.6,0.8 and 1 wt%) for desirable characteristics [6]. Additionally, carbon nanofiber (CNF) and Nano-Fullerene (C60) were tested at the same weight percentage [6]. The desirable characteristics tested include viscosity, permeability, dropping point, corrosion, evaporation loss, humidity resistance, extreme-pressure properties and resistance to fuel, water, and aqueous alcohol [6]. Upon testing, it was found that resistance to fuel, water and aqueous alcohol was increased among all nano greases, for after immersion of the greases in the tested solutions for 7.0 hours +/- 0.5 hours and drying for one day, no swelling, cracking, or blistering was observed [6]. This is due to carbon's hydrophobic property in aromatic structures such as graphene sheets, which make up the composition of carbon

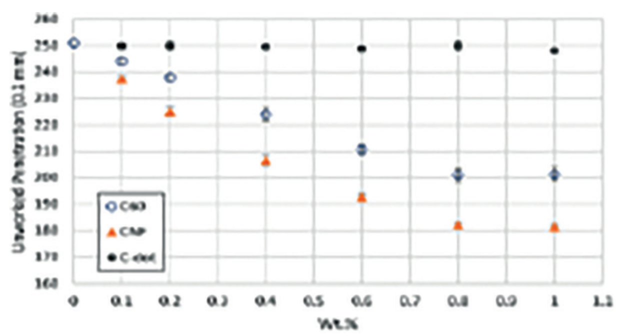

Figure 1- Percent Weight versus Unworked Penetration Reprinted from [6]

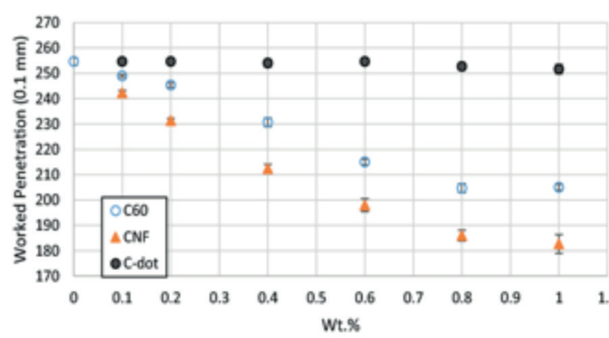

Figure 2- Percent Weight versus Worker Penetration Reprinted from [6]

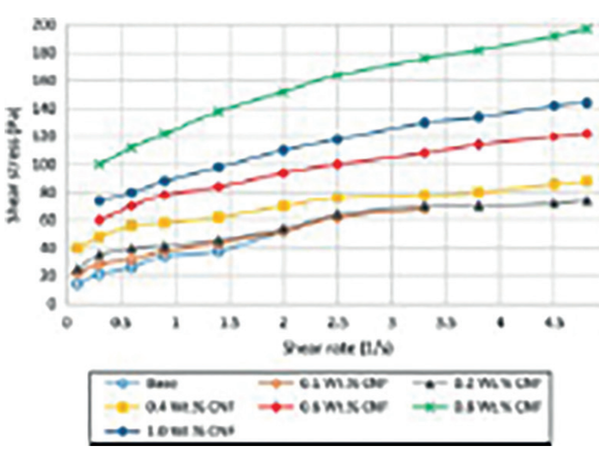

Figure 3-Shear rate versus Shear Stress Reprinted from [6]

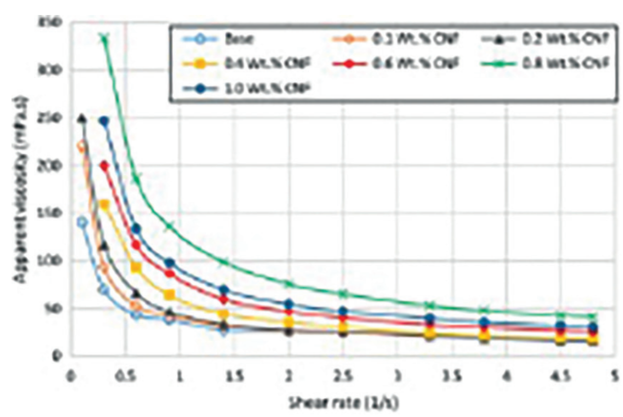

Figure 4-Shear Rate versus Viscosity Reprinted from [6]

nano fibers [7]. This resistance to water and fuel is especially important in the application to EVs, where this resistance will improve the life of both the grease and the bearings it is applied to. This will save time and money for the consumer, as they will spend less to replace bearings, as a larger time between maintenance will be observed. Other improvements, specifically in viscosity and penetration, were also found to be greatest in the CNF nano greases and the optimal nano greases were found to contain "CNFs with weight percentages in the range of 0.4-0.8" [6]. This decreased penetration is due to the CNF becoming an interwoven fiber, which increases resistance against gas passing

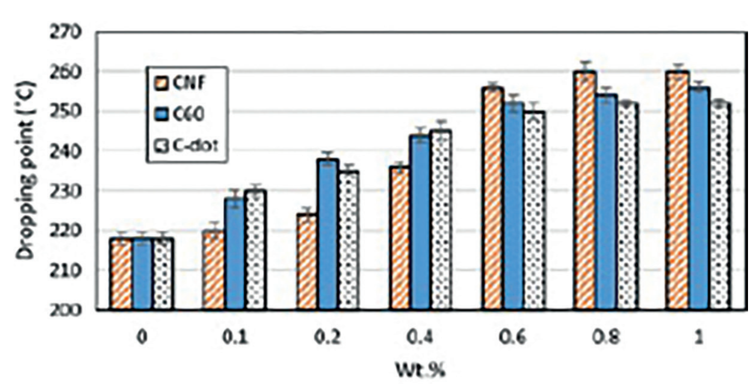

Figure 5- Percent Weight versus Dropping point. Reprinted from [6]

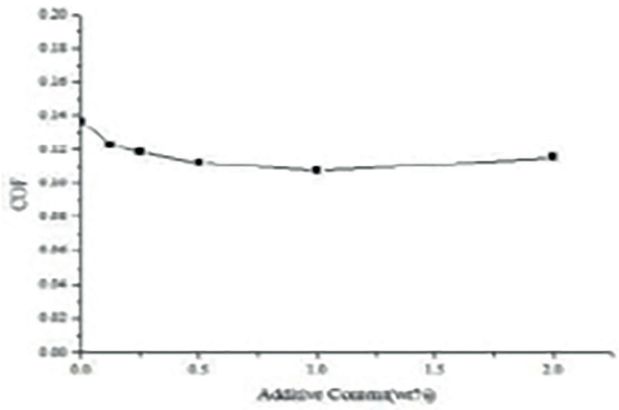

Figure 6-
Additive Content versus Coefficient of Friction
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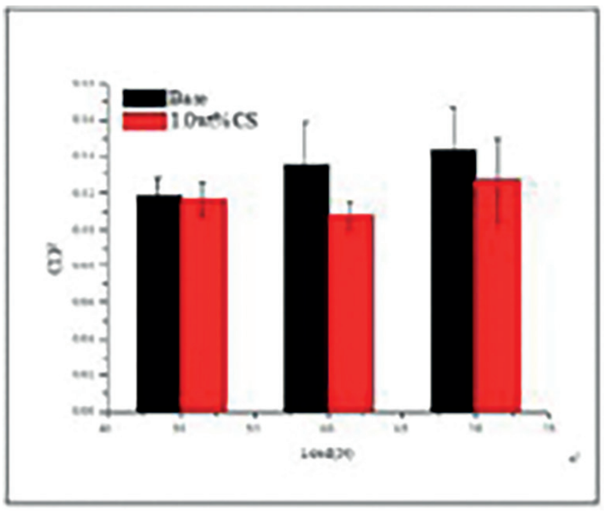

Figure 7-
Load versus Coefficient of Friction
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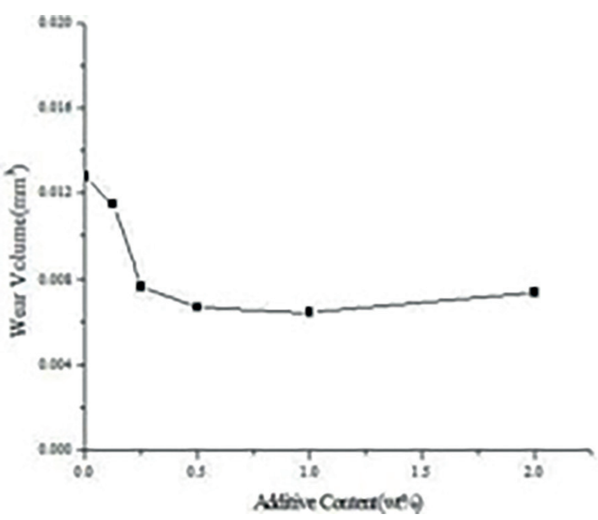

Figure 8-
Additive Content versus Wear Volume
Reprinted from [13]

through the material due to an increase in mean free path of the gas [6]. The interwoven fibers cause an increase in the distance between collisions of the grease and gas particles [8]. The grease is then penetrated at a slower rate than base grease in the same time interval and is shown in both worked and unworked grease. A more profound decrease in the penetration was shown in the worked grease, which refers to grease that has been extensively disturbed, usually in a piston. The results for both worked grease and unworked grease are shown in Figures 1 and 2, respectively.

The interwoven fibers directly increase the consistency of the nano grease, making it thicker [6]. This thickness explains the heightened viscosity shown in Figure 3, which represents the shear rate versus shear stress. This plot highlights the CNF grease's ability to endure greater shear stress than base lithium grease at the same shear rate, meaning, the CNF grease is more resistant to shear and can undergo greater pressure and harsher conditions. A reduction in viscosity is also seen in Figure 4, which plots the Shear Rate versus Apparent Viscosity. A clear exponential decay plot is shown, with the viscosity decreasing as shear rate increases. This decay is expected due to lithium grease being a non-Newtonian fluid, which is characterized by a decreasing viscosity with an increasing shear rate [9]. However, the apparent viscosity of all nano greases is higher than the base lithium grease at the same shear rate. A higher viscosity grease has a higher consistency, which therefore gives the grease greater structural strength [10]. This property is reinforced by the resistance of the CNFs to penetration discussed previously.

Not only is viscosity and resistance to shear higher, but Figure 5 accentuates how the nano greases, specifically the CNF nano greases, have increased dropping point temperature on the interval found to be optimal (CNF 0.4-0.8% wt). The dropping point is defined as "an indicator of the heat resistance of the grease and is the lowest temperature in which the oil can flow and the phase of grease changes from semi-solid to liquid" [6]. In other words, the dropping point is the maximum temperature at which the grease remains completely functional at a specific condition. By increasing the dropping point, the temperature range in which the grease can function is increased. This heightened dropping point is desirable for the high temperatures that can be reached in an EVs electric motor bearing [11]. Additionally, this increased range allows for a broader assortment of applications and sustainability across harsher conditions, making the grease more desirable. This improved dropping point stems from the stronger structure of nano greases, as the interwoven fabrics and resistance to water and fuel give a higher consistency. This increased consistency allows for the structure of the grease to remain intact even in higher temperatures and resistance to higher temps directly increases the dropping point. It is clear from the plot in Figure 4 that lithium grease synthesized with CNFs over the weight percentages of 0.4 to 0.8 produce improved dropping points even among nano greases. CNFs and nanotechnology, in general, greatly improve lithium grease and its application in electric vehicles.

Although electric vehicles are viewed as the 'cleaner' alternative to internal combustion engines, questions are being raised about the cleanliness of the greases utilized in the vehicle. Lithium greases are used for an EV's powertrain, which is responsible for taking energy stored in the battery system of the vehicle to the motors, as well as lubricating doors and hinges [12]. Lithium grease will be an essential player in moving to a cleaner, more efficient electric vehicle. As such, researchers aim to answer questions about the grease's environmental friendliness and possibly improving it. One solution to this question is contained in the research of Tingting Li et al., whose research tested lithium greases containing eco-friendly carbon microspheres at different percent weights (0%, 0.0625%, 0.125%,0.25%, 1%wt, and 2% wt) [13]. These eco-friendly carbon spheres (CS) were prepared using one step hydrothermal carbonization of glucose, in which glucose was dissolved in distilled water under magnetic stirring [13]. Upon testing the tribological behavior, it was found that the inclusion of 1% wt at the load of 60 Newtons yielded a reduced coefficient of friction of more than 20 percent compared to the base lithium grease, as shown in Figure 6 [13]. A system comprised of a steel disk and steel ball was used in this test, where the ball is under a load that can be varied between trials (in this case 50, 60, 70 N) [13]. The results of this test are shown in Figure 7, which represents the average coefficient of friction of both base lithium grease and 1 % weight CS grease versus load [13]. It is clear the greatest reduction in coefficient of friction came from the 60 Newton load, where there was a 21.35% decrease in coefficient of friction between base and 1% weight CS.

This decrease in the coefficient of friction directly reduces the wear volume. The wear volume is an analysis of the wear of a surface due to friction [14]. The results are shown in Figure 8 and visibly represent a vast decrease in wear, with minimum wear occurring at 1 percent weight [13].

This decrease in wear is due to the micro roller characteristic of the carbon spheres. These spheres act as nano scale ball bearings, reducing friction while simultaneously forming and reinforcing the protective film between the contact surfaces [13]. This phenomenon is shown in Figure 9 below.

This reduction of friction is due to the converting of sliding friction into rolling friction caused by the carbon nano spheres [13]. This conversion moreover decreases wear on the surfaces, increasing the lifespan of the surfaces. This anti-wear effect is shown in the comparison of Figures 10 and 11, which show the wear on the surfaces after testing. It is visibly clear that the wear on Figure 10 was significantly less than the wear on Figure 11. It is then safe to say that Surface Y would last longer than Surface X in real-life application, for the rate at which the surface would deteriorate is lower in Y than in X. Surface Y represents the surface of the disk after the testing of the 1 % wt nano grease, and Surface X is the surface of a separate disk under the same load (60N), after testing of the base grease.

Therefore, not only did these CSs make the grease more environmentally friendly, but they also vastly increased efficiency and life span of the lithium greases, for reduced wear coincides with performance retention. This method of preparation of lithium greases, which are used heavily in electric vehicles for the powertrain, not only makes the greases eco-friendly but also improves upon the performance retention and sustainability of both the grease and the contact surface.

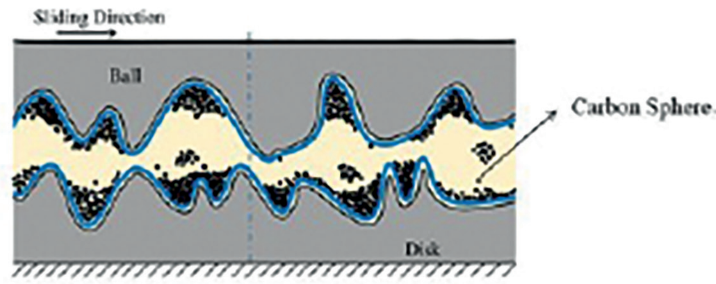

Figure 9-
A visual representation of the CS nano greases ability to act both as micro rollers and a reinforcer of the protective film between contact surfaces.
Reprinted from [13]

While EVs are the future, 2035 is still a long way away and one state's ban on internal combustion engines (ICEs) does not lead to the end of the ICE industry. Additionally, lithium grease is not exclusively used in EVs, as a recent NLGI Grease Production Survey estimates 70 percent of the grease sold worldwide is based on simple lithium or lithium complex thickener [15]. Increasing the performance of lithium grease is thereby integral to the growth and success of the lithium grease industry, as well as its sustainability. This desire for increased performance can be found in the research of Adam Rylski and Krzysztof Siczek, who examined the effect of the addition of ZrO2 on the tribological behavior of lubricants. Lithium grease with and without ZrO2 additive is discussed as well as the chemical processes of agglomeration and aggregation [16]. The mechanism of these processes are shown in Figure 12.

Both processes refer to the clustering of particles, with the main difference being aggregation is reversible while agglomeration

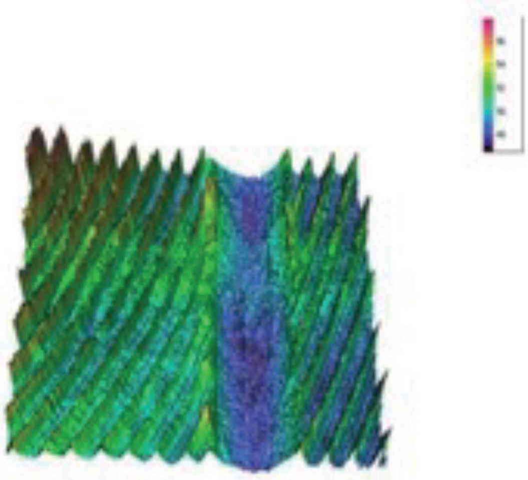

Figure 10-
The contour map of the surface and corresponding grinding depth of the surface used in the testing of 1 % wt CS nano grease.
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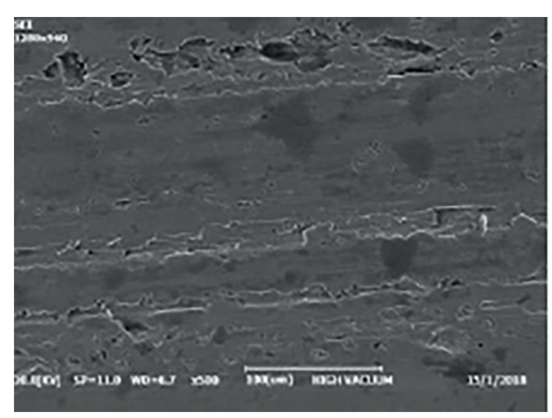

Surface X – the desktop scanning electron microscope representation of the surface corresponding to the base grease test.
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Surface Y – the desktop scanning electron microscope representation of the surface corresponding to the 1 % wt nano grease test.
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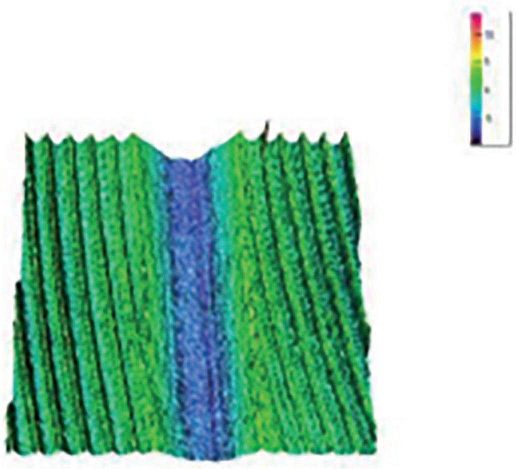

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Figure 11- The contour map of the surface and corresponding grinding depth of the surface used in the testing of the base grease. Reprinted from [13]

Advanced Solutions International, I., & Renessler, J. V. (2015, September). Lubricants for the nuclear power industry.

is not [16]. Both types of clustering were additionally tested, and the results are shown in Figure 13, which is a plot of the load in the contact zone versus the coefficient of friction. These results clearly show that the lithium grease containing 1% ZrO2 without agglomerations outperforms the lithium grease, yet the grease with the ZrO2 with agglomerations is outperformed by the basic grease. Therefore, the non-agglomerated ZrO2 is most desired, and this product can be obtained by using the commonly used precipitation method, which yields aggregated ZrO2, which is then disaggregated by ball-milling commonly found in a ball bearing system. This product will allow for the desired performance of lithium grease with 1%wt ZrO2 outperforming the base grease.

Lithium greases and their vast applications represent the current trends of nanotechnology's application in lubricants. With electric vehicle production on the rise due to federal rulings and the threat of climate change, these heavily sought-after products will require the lubrication that greases and their additives provide. These greases and lubricants will need to be efficient both monetarily and in the application, as companies will look to minimize cost and maximize product quality. To achieve this, research has shown time and again nanotechnology will be the basis of this maximization of quality.

Researchers always look towards the future and possible avenues of more in-depth study. One such avenue that arises in this paper comes from the works of Sadeghalvaad et al. Though heavily discussed in this paper, this avenue of research is still in the beginning stages. Some possible continuations of this research could include the further investigation into the effect on acidity and alkalinity of the greases upon addition of the nanoparticles. Changes in these properties could be the true driving force for the change in consistency and dropping point, and the nanoparticles themselves almost insignificant in the effect. Therefore, further research into the effect CNF, C-dot, and C60 nanoparticles have on acidity of lithium grease should be further investigated, for both economic and ecological purposes.

Additionally, the dropping point for lithium base grease is generally observed around 190 degrees C as determined by ASTM D566. In the research of Sadeghalvaad et al., the dropping point is observed in the range of 215-220 degrees C. This discrepancy is yet another possible improvement that can be investigated in this avenue of research, and opens the door for future workings and experiments.

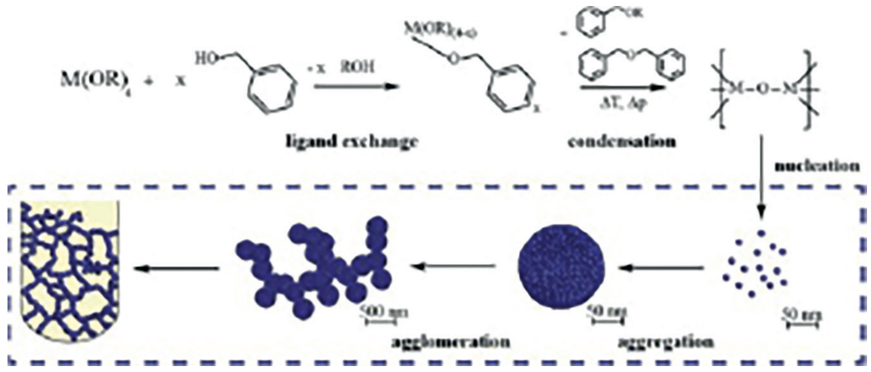

Figure 12- A visual representation of the mechanisms behind the agglomeration and aggregation processes. Reprinted from [16]

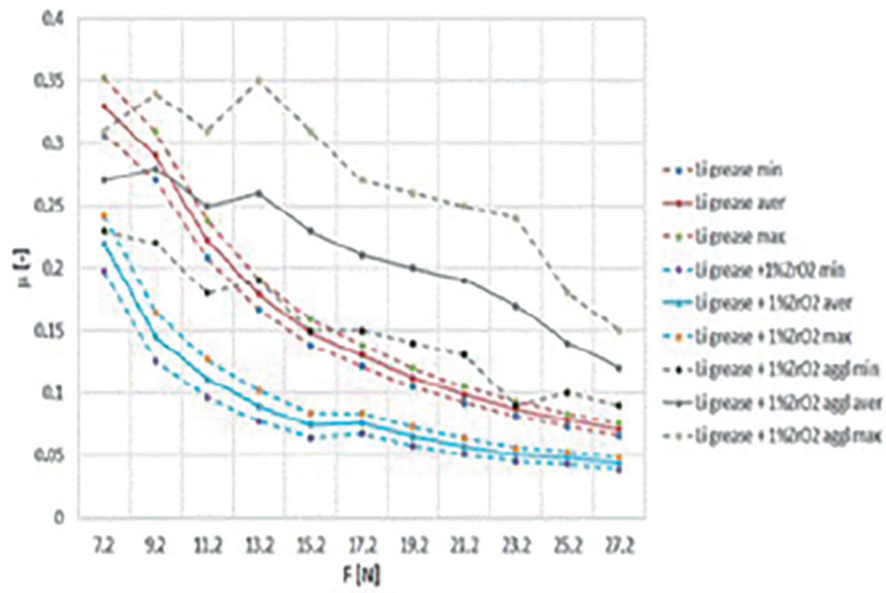

Figure 13- Carrying Load versus Coefficient of Friction. Reprinted from [16]

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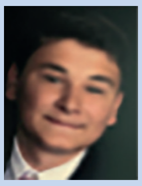

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