Nanoparticle Additives for Improving Lubricant Performance

Xinghe Ye*

School of Engineering, University of Edinburgh, Scotland, EH9 3JW, United Kingdom

* Corresponding Author Email: s2040848@ed.ac.uk

Abstract. The lubricant is an important industrial product widely used in vehicles and other machines. The main purpose of a lubricant is to reduce friction loss and save energy. However, with the development of the vehicle, the appearance of electrical vehicles, for example, and machines, lubricants need to satisfy more demands. Normally, this was fixed by adding additives. Nanoparticles are one of the best additives because they can efficiently reduce friction loss and provide a more useful function. But nanoparticles may form sedimentation in lubrication, which will increase friction loss and cause damage. Common methods like stirring, ball milling, and chemical methods are used in lab production to keep particles stable in lubricant. All those methods can form relatively stable samples of nano lubricants, but it is still hard for industrial manufacturers because of the technology blank and high cost. Nano lubricant is a potential market and can save more energy in the future.

Keywords: Nanoparticle, Lubricant, Additive, Electric vehicle.

1. Introduction

Lubricant is a significant industrial product that can decrease machines' processing costs and lead to less energy loss. Early lubricant is the side-product of purifying oil. With further study and improvement, lubricants have better performance and different special functions (anti-freeze, anti-oxide). As the main lubricant oil market, the vehicle industry closely relates to it. Mostly, the improvement of lubricant is the solution for vehicles' needs. Now, internally combusted engine vehicles (ICEVs) are gradually out of the mainstream, and electrical vehicles (EVs) are the new future for the vehicle industry. Thus, lubricants need better improvement to satisfy EV requirements. Unlike ICEVs, EVs do not include many components that must be lubricated. However, EVs' specific components still need lubrication, such as the gearbox. Although the EVs do not require more lubrication, they need better lubricative performance and some special functions to overcome the environment of EVs.

Nanotechnology, mostly nanoparticles here, studies particles' properties with nano diameter. By adding nanoparticles into a lubricant, the key performance of the lubricant, anti-friction, is significantly improved. While another function appears, like anti-oxide. Nanoparticles have geometry properties that decrease friction between gear and metal surfaces in several ways. Compared to other methods like changing the composition of lubricant, nano additives have obvious advantages in amelioration.

Although nanolubricant has better performance, its production is still hard. For the experiment, a small value of the sample is produced. Since then, the synthesis has been relatively easy but needs a special method to keep nano-particles stable in lubricant oil, and it always takes a long time. Industrial production is more complicated: how to keep oil stable and decrease the cost to decrease the price. Nano additives are a potential method for lubricants. Performance improvement still needs more research.

2. The improvement of lubricant performance by nanoparticles and mechanism

Lubricants are a significant industrial product for vehicles; they increase the engine's efficiency and protect engines from prolonging their service life. With additives, lubricants can achieve different

purposes. As additives, nanoparticles improve lubricant performance through their geometric properties.

2.1. Reduce Friction Between Moving Parts

2.1.1. During Engine Operation

If components that move relatively have a contact face without lubricant, the heat generated by instantaneous motion can melt the components. Lubricant will cover the contact face and form a protection film, decreasing the friction coefficient. While adding nanoparticles will create disparate effects, which are decided by the nanoparticle's types. From Figure 1, there are six positive roles of nanoparticle additives. Role (a) rolling, (b) forming a protective film, and (c) mending are common. Also, forming a protective film is the domain mechanism [1].

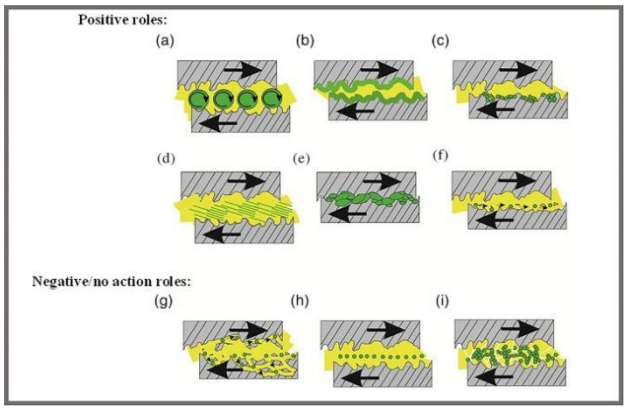


Figure 1 rolling, protective film and mending [1].

2.2. Absorption of Heat and Refrigeration

Since the internal combustion engine has limited efficiency, the heat generated by fuel is consumed for power output and overcomes friction loss partially. Excess heat inside the engine must be disposed of without the heat discharged into the atmosphere. Otherwise, the heat will burn the engine and lead to irreversible damage. Lubricant will absorb some heat and help the system discharge the heat. With nano-particles additives, the ability of refrigeration will significantly improve. For instants, by adding CuO nanoparticles into R134a, the heat transfer coefficient will increase by 61% [2]. The application is based on the theory of Maxwell's mixture states, which indicate that the thermal conductivity of liquid will increase with solid particles' suspension. At the same time, because the need for vehicles is different, multiple choices of nanoparticles can be used.

2.3. Inoxidizability

Lubricant will react with gas and NO_1, NO_2 and SO_2 under high temperatures, especially for electrical vehicles with higher temperatures. The oxidational temperature increased by adding nanoparticles. For instance, the experiment group chooses SNCF as an oil sample and assesses the temperature when the sample begins oxidation. In Figure 2, with different diameter nanoparticles added, the oxidation temperature increases from about 15°C to 30°C [3]. A possible explanation is a nano-absorbing mechanism. The nanoparticles will break the reaction chain and prevent oxidation, like free radicals' collectors [4].

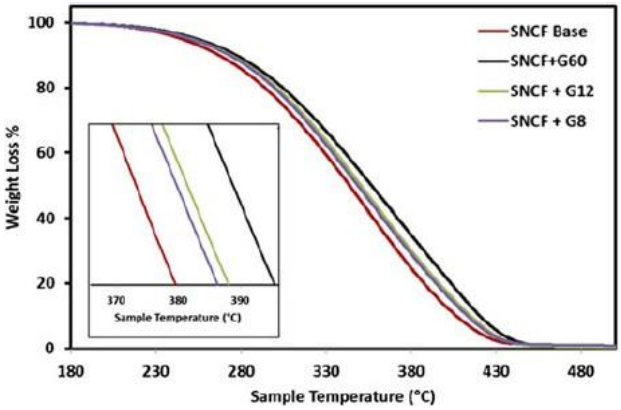


Figure 2 oxidation temperature curve [3].

3. Fabrication strategies of nanolubricants

The surface of nanoparticles is relatively large, which leads to the hardness of manufacturing nanolubricants. A large surface area will lead to intermolecular force and decreased stability. The manufacture of nanoparticles is relatively mature, but the nanoparticle additives are limited. But there are still several ways to enhance stability.

Although nanolubricants are industrial products, most productions are in the lab, which is used to find their properties. For lab fabrication, the cost and time can be neglected because the demand is low. This means most manufacturing method in the lab is unreasonable for huge industrial manufacture, but through this lab manufacturing method, we can find the path for huge industrial production.

3.1. Physical Methods

The most common method is the physical way. Through equipment, relatively stable lubricants can be produced. However, the physical way mostly takes a long period, like a month. The commonly used method include stirring, ball milling and sonication.

3.1.1. Stirring Method

With Brownian motion, random motion for small particles, nanoparticles can remain in dispersion status at the beginning after being added to the lubricant. But they will form sedimentation because of gravity, and sedimentation is undesirable. The large size of sedimentation will not reduce the friction but increase it. The stirring method can increase dispersion stability and reduce sedimentation [5]. The method is straightforward, using rotation to increase particle motion. But it is quite efficient. In Figure 3, both samples are nano-particles MoS_2 lubricants. The yellow line presents the sample not stirred; its friction coefficient increases with cycles and reaches about 0.18. The green line present stirred sample. It stirred from 0 to 72000 cycles, and there was a stable period from 72000 to 150000 cycles. Then, after the second stirring time, its friction coefficient reaches about 0.06 and remains stable, far lower than the stirred sample [6]. This experiment proves that the stirring method is quite a useful method.

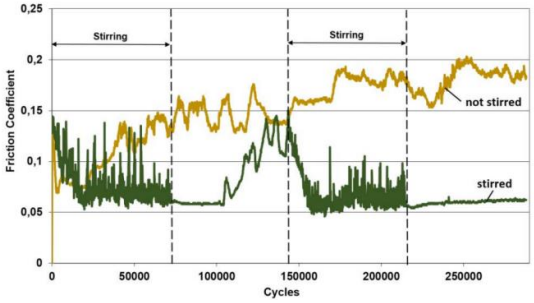


Figure 3 Performance of LC-type IF-MoS_2 [6].

3.1.2. Ball Milling and Sonication

Except stirring, ball milling equipment is also a common device. Ball milling equipment is a cylinder containing plenty of small spheres. During the cylinder rotation, small spheres will collide and promote blending. In the experiment on Cu nanoparticle additives, Yu and his team used high-energy mechanical ball milling agitation to provide dispersion stability of Cu nanoparticles in oil [7]. The ultrasonic probe is also widely used. The oxide nanoparticles were dispersed separately by the ultrasonic probe for instants and vegetable base lubricant preparation [8].

3.2. Chemical and Self-Dispersed

Through chemicals, nanoparticles' surfaces can be modified, increase dispersion stability, and form more stable lubricants. For example, organic chemicals can be used for inorganic nanoparticles. The chemical method can form a stable lubricant for a long period, like 30 days or better but the most important staff: structure of nanoparticles can be decomposed by the functional groups, and there is still the possibility of pollution and harm, so it is not a clean and safe method [9].

The self-dispersed method means rearranging nanoparticle additives' structure; several research studies have proven that the dispersion stability will increase by regulating nanoparticles. Dou et al. compare crumpled graphene balls with graphite, r-GO and carbon black, all 0.1 wt.%, see Figure 4. After 20 hours, all samples show obvious sedimentation symptom without the crumpled graphene balls, which prove that the crumpled graphene balls have good self-dispersion properties. The attraction force between particles has been reduced [10]. Self-dispersion method is an eco-method with a better future that needs further study.

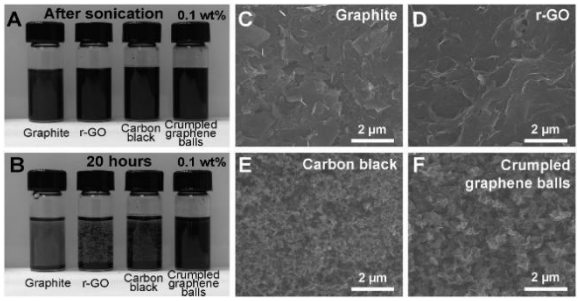


Figure 4 sedimentation symptom of graphite, r-GO, Carbon black and graphite ball[10].

4. Recent progress of nanolubricants for vehicles

There are three kinds of lubricants: mineral-based, synthesis-based, and bio-oil. Each of them varies depending on the production process. Several research teams choose a different sample and add nanoparticles, then evaluate their performance.

4.1. Mineral-Based Oils

Mineral-base oils are refined by crude oil. It is one of the most important side-products for oil refinement and is the most well-known and common oil. As the earliest used lubricant oil, its quality mostly depends on the refinements' level. Research shows its wear scar diameter performance has improved after adding metal nanoparticles.

Svajus J. Asadauskas and his research team design the experiment to find the nanoparticle effects on mineral oil. They add nanoparticles of copper (Cu), iron (Fe) and zinc (Zn) at 0.01%, 0.1% and 1% treat rates separately. (Svajus J. Asadauskas et al. 2015) Figure 5 shows the relationship between the added particles, temperature, and wear scar diameter [11].

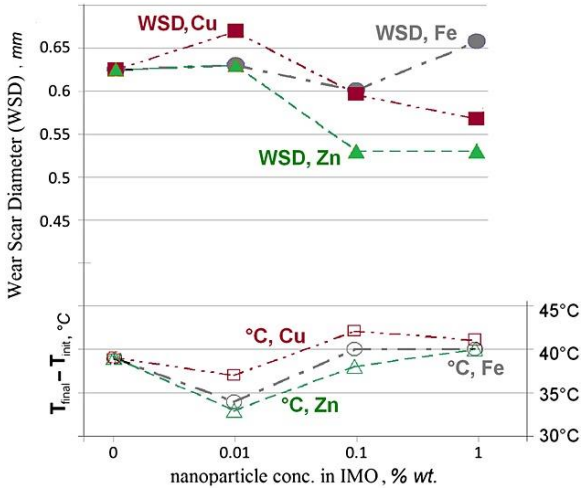


Figure 5 Effect of Cu (squares), Fe (circles) and Zn (triangles) curve of different concentrations in mineral-based oil[11].

This experiment has two key points: wear scar diameter and temperature. Wear scar diameter, WSD, is the length of the scratch. If the mutual friction is intensive, the WSD will be large and cost more friction loss. Meanwhile, heat is also undesirable. Much heat will generate damage. Ideally, additives can reduce WSD and heat.

The temperature change is relatively negligible, meaning heat resistance is not an obvious performance for these samples. Metal nanoparticles will not increase the heat resistance of this mineral-base oil. However, the wear scar diameter has a relatively large difference. Protection for wear scar for nano iron is not obvious, with WSD floating around 0.6 to 0.67; wear scar diameter does not have a clear relationship with nanoparticle concentration. However, with the increasing nanoparticle concentration, nano copper and nano zinc show great protection for wear scar. Both copper and zinc additives decrease the wear scar diameter while zinc is better. From 0.01% to 0.1%, adding nano copper or nano zinc decrease WSD for 0.1mm. Although the scale is tiny, friction constantly occurs in a real application. This means even a tiny improvement can reduce lots of loss.

Furthermore, the team scans two samples of the example; see Figure 6. The sample with Zn nanoparticles is on the top, and the bottom is not. The wear scar diameter is 1.3mm shorter for nanoparticles adding oil sample. The scratch is clear on the no nano-particles sample [11]. If severe damage occurs, subsequent injuries will only intensify since the surface is no longer smooth. Friction loss will increase.

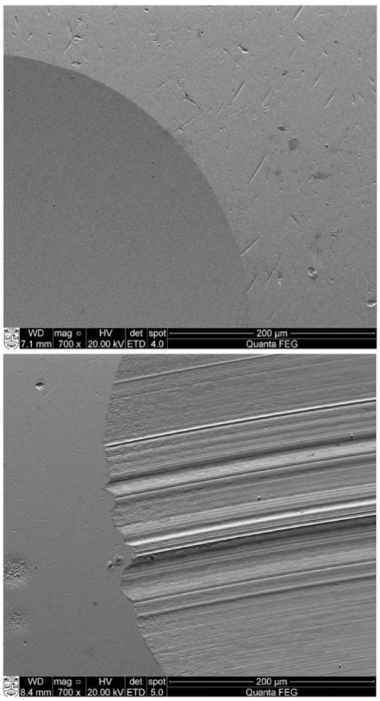


Figure 6 microscopy of samples, top with additives and bottom without additives [11].

4.2. Nano Synthetic-Based Grease

Synthetic-based grease, unlike mineral-based oil, replaces the base oil with easter and adds other additives. It normally performs better than mineral-based oil but is a reprocessing product. Same as with mineral-based oil, nanoparticles can improve their performance.

A research team from the National Taipei University of Technology experimented to find the anti-wear and friction properties of adding nanoparticles (specifically CuO and TiO_2) into Lithium Grease [12]. Experimental results prove that the nanoparticles will keep friction coefficient in a relative low zoon compared with pure lithium grease; experiment data are shown in the following charts:

After the first increase because of metal-metal contact, lithium grease with nanoparticles performs better in keeping the friction coefficient. If the friction coefficient keeps increasing and holds in a relatively high zoon, more energy will be wasted in a real application. That means nanoparticles adding can save energy. Moreover, when the percentage of nanoparticles increases in grease, the grease performance will be improved. Take 0.5 wt.% and 2.0 wt.% CuO as an example. The latter can keep the friction coefficient between 0.03 to 0.035, which is about 0.01 better than 0.5 wt.% CuO lithium grease.

Figure 7 shows the relationship between sliding time and friction coefficient, depending on different concentrations of nanoparticles, separately for TiO_2 and CuO [12]. The friction coefficient increases with time, so more friction loss is generated. Both nanoparticles decrease the friction coefficient. They have the same trend. For the big picture, TiO_2 particles have better performance. No matter what concentration, the friction coefficient is lower than the pure grease, in which CuO 2.0 wt.% has a larger friction coefficient than pure grease at the beginning. The friction coefficient decrease does not have linear relationships with concentration, which means high concentration nanoparticles do not mean less friction loss. For example, 1.0 wt.% TiO_2 has the best performance. More nano-additives do not always mean better.

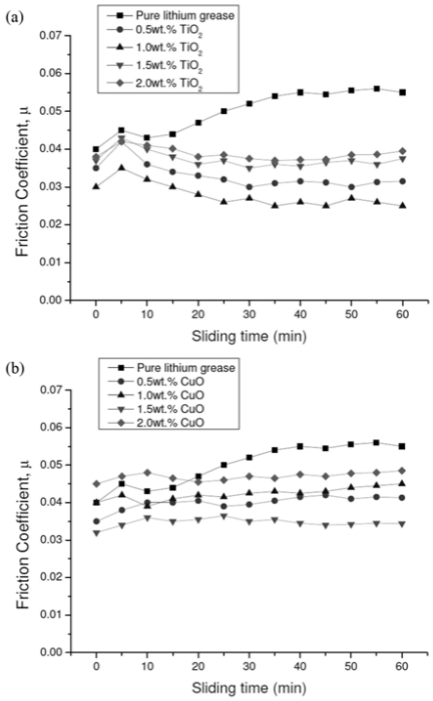


Figure 7 Friction coefficient of TiO2 and CuO [12].

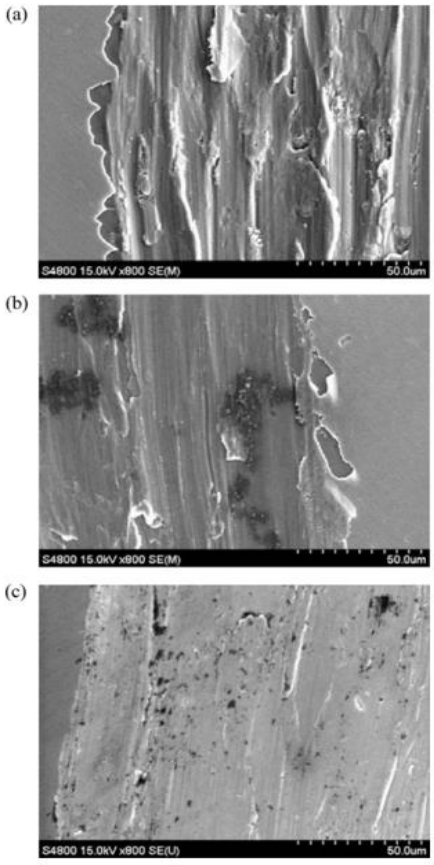


Figure 8 Micrograph samples of pure lithium grease (a), lithium grease + TiO_2 (b) and lithium grease + CuO (c) [12].

The team also scans the sample, see Figure 8. Sample (a) has clear scratches, which are irregular, leading to worse friction loss if you keep using it. By lubricating by nanoparticles, (b) and (c) show smoother surfaces than (a) [12].

4.3. Nano Bio-Grease (Vegetable Grease)

Vegetable grease, or bio grease, is an eco-production. It is refined from plants, different from mineral and synthesis-based oil. Compared to mineral-based and synthesis-based oil, bio-grease is greener and environmentally friendly. Also, nano additives can improve their properties.

Ankit Saxena's research team design the experiment to find the relationship between the concentration of nanoparticles and the grease performance. They use soybean oil as base oil, organo-montmorillonite as a thickener, and $CaCO_3$ nanoparticles as additives. See Figure 9. By adding nano $CaCO_3$ into vegetable grease, the consistency of the greases will increase when the concentration of nanoparticles is 0.5% or 1%, and the consistency of the greases increases [13].

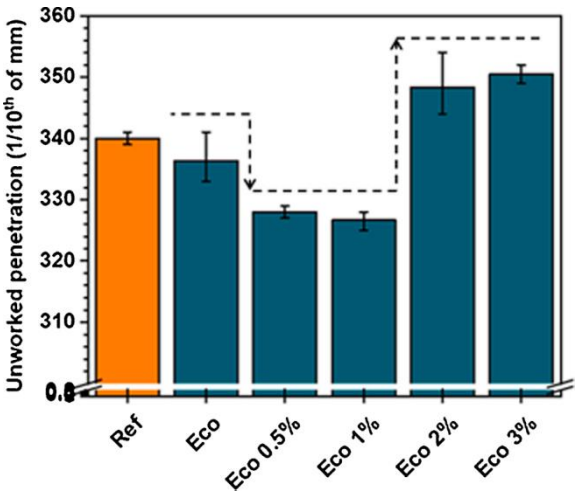


Figure 9 Consistency of newly developed gels/greases [13].

Lower concentration nanoparticles can improve the strength of the microstructure of the grease because of the intermolecular force. But when the concentration keeps increasing to 2% or higher, repulsions will decrease the strength. A schematic diagram is presented in Figure 10 [13].

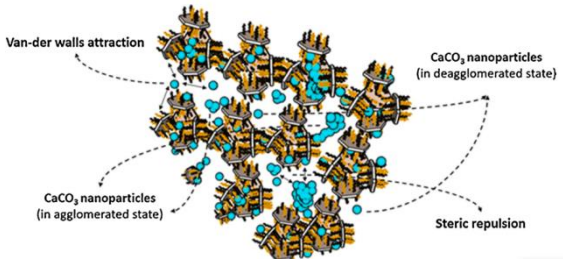


Figure 10 Diagram illustration [13].

For other nanoparticles, the bio-oil also shows better performance. In another part of Svajus J. Asadauskas' study, the team adds Cu, Zn and Fe nanoparticles into rapeseed oils. Figure 11 shows the wear scar diameter of different samples. By increasing the concentration of nanoparticles, all samples show a decrease in wear scar diameter except for Zn, its WSD rising for concentration increasing from 0.1 to 1. Nano Fe particles perform best, decreasing WSD by about 0.1mm [11].

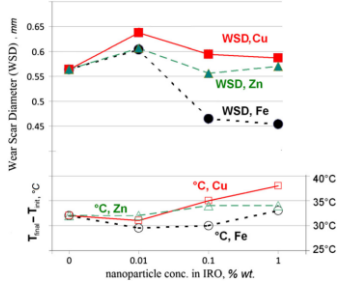


Figure 11 Effect of Cu (squares), Fe (circles) and Zn (triangles) curve of different concentrations in bio-oil [11].

5. Conclusion

Lubricant, an important industrial product, is improving over time to satisfy the demand for improving vehicles. But the vehicles need not only better basic lubrication like reducing friction loss, but they also have new demand. For example, the electrical vehicle needs electrical resistance and high-temperature resistance. Lubricant needs additives to get a new property. Nanoparticles are one of the best choices because their great variety can provide vast new functions, just like the three tractional oil and grease.

The three common greases on the market can improve tribological and thermodynamic properties by adding different nanoparticles. These properties are extremely important for electric vehicle greases, which can better overcome the problems in the operation of electric vehicles, and it is foreseeable that nano greases will become popular products in the market in the future.

But the cost and industrial manufacture are still problems, most experiments use a small number of nanolubricants that do not need long time stabilization, but as an industrial product that will make the sale on the market, it needs to be better. After having a mature industrial manufacturing method, the cost will be high. Then the environmental problem will appear. In the future, massive production and usage will need further study.

Nano lubricant is an untapped area, although some nano-oils already exist on the market. There is still a huge blank because of the hardness of industrial manufacture. As we all know, vehicle oils and lubricants are primarily side products in refining petroleum. Adding nanoparticles is an extra cost. But the need for better lubricants is created by developing vehicles or electric vehicles. Faster and more heat for the engine is a problem for the new generation of nanolubricants.

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