Developments in lubrication efficiency through nanotechnology

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Introduction

The lubricants industry is focused on developing more environmentally friendly oils, with increased energy efficiency, critical to control wear and metal fatigue in severe conditions, such as those present in wind turbines.

Whilst reduced viscosity oils have been used to improve the fuel efficiency of lubricants, this can cause an increased risk of wear and metal fatigue. New technical solutions are required that not only reduce friction, but also take into account and control these considerations.

The latest nano technologyis a significant breakthrough in lubrication that can help the environment by improving energy efficiency cutting emissions, and reducing the carbon footprint. It can also improve the durability of highly stressed mechanical systems as part of the Green revolution and enable further reductions in ZDDP (Zinc dialkyldithiophosphate) in lubricants, to improve the performance of engine exhaust aftertreatment systems.

Health & Safety

Concerns have been raised about the use of nanomaterials and the risk to human health and the environment, however, new technology now enables nanoparticles to be produced in-situ and dispersed in micelles, within a stable colloid in oil. so the additives do not contain discrete or isolated particles. They are, therefore not classed as nanomaterials, which is in accordance with the European ATC (Additive Technical Committee). These additives are compliant with European REACH and CLP regulations, and are REACH registered by the European Chemicals Agency (ECHA).

Friction

One of the important performance features of these new additives is that they are very effective friction modifiers. Friction occurs when two moving parts make contact. Lubricants form a fluid-film between the surfaces (hydrodynamic lubrication), but in stressful conditions this fluid-film collapses and cannot keep the surfaces separated, and metal-metal contact occurs. Friction modifiers adsorb on metal surfaces to form a tribofilm that has low shear strength and reduces friction.

There are two main types of conventional friction modifiers. Organic, and metal-containing compounds, for example molybdenum. The molybdenum-additives are generally regarded as more effective. However, both types are sacrificial and deplete to lose performance. The wear performance of these additives is also relatively poor because the adsorbed tribofilms brush off metal surfaces. There is clearly a shortfall in existing friction modifier technology that must be addressed.

There are also many other additives, for example boron and ceramic, claiming to improve fuel economy and wear protection, but they have not all been thoroughly tested to substantiate the claims.

Wear

Another important performance feature of the new additives is that they are very effective anti-wear agents. Wear occurs when moving parts make contact, due to the inability of the lubricant film to keep the surfaces separated. Metal-metal contact occurs, which causes abrasive wear. The increased use of lower-viscosity oils makes wear a more serious problem, because of the reduced film thickness.

There are many types of conventional anti-wear additives, based on different chemistries. However, they are not effective in very stressful systems such as wind turbine gearboxes. The most common additive is ZDDP. It has significant shortcomings because it is sacrificial, depletes rapidly, and loses effectiveness over time. A further problem is that ZDDP actually increases friction and reduces energy efficiency.

Tribofilms

Tribofilms are thin layers of lubricant on stressed metal surfaces, and play very important roles in reducing friction and wear protection. Copper nanoparticles are known to form very effective tribofilms, because they adhere strongly to metal surfaces.

Copper Nanoparticles

There is currently a lot of research being conducted with copper nanoparticles, especially by the Russian scientist D. N. Garkunov, who found that copper particles reduce friction and wear, and also repair damage to metal surfaces.

Many researchers have tried to produce copper nanoparticles for lubricants, but they did not perform well in actual field applications, proving unstable and difficult to disperse in oil. Surfactant capping was attempted but with limited success. The key problem is that the particles agglomerate together to form sediments, and cannot be used in commercial oils.

Performance Demands

The OEMs (Original Equipment Manufacturers) have many unmet performance needs with conventional friction modifiers and anti-wear additives. A new type of friction modifier is required to form robust tribofilms that are sustainable. New anti-wear additives are required that not only reduce conventional wear, but also prevent WEC (white etching cracks) and metal fatigue. This is key to longer oil change and maintenance service intervals.

Nano-Additives

Companies, including Nanol Technologies, are now developing effective lubricant additives, which meet OEM performance demands. The breakthrough is that the additives contain dispersed copper nanoparticles, which are completely oil soluble. The novel technology involves copper-based organometallic salts in combination with an activated complex, to form of copper nanoparticles in-situ. The particles are

dispersed in reverse micelles, within a stable colloid.

The nano-additives form very effective tribofilms on metal surfaces. They give instant friction reduction and lower wear. These positive effects are sustained on a long-term basis. As the tribofilm is worn, new replacement layers are formed, which is part of the self-healing process. Copper was found at a depth of 10 nm in the metal sub-surface. This shows that copper diffuses into the metal surface to prevent white etching cracking (WEC). Studies have also shown that the nano-additives function independently and do not interfere with other additives in lubricants.

Performance Verification

Theadditives have been independently tested to verify the performance. This work was carried by Professor Scherge, at the Fraunhofer IWM MikroTribologie Centrum, in Germany. The formation of copper tribofilms was also investigated and a multi-phase wear and friction reduction mechanism was observed.

Test Results

The thin tribofilm formed by the additive was examined (Figure 1). Several circular spots with lower friction were detected.

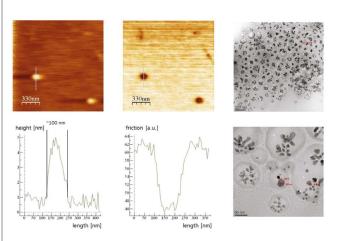


Figure 1. Left & Centre: AFM images of wafer surfaces with Nanol additive. Right: Transmission electron images of copper nanoparticles.

The copper nanoparticles were also studied (Figure 1). The larger circles are micelles and the dark cores are the copper nanoparticles. This confirms that the particles are dispersed in a colloidal suspension.

The wear tracks on a steel disk were studied. The border between protected and worn areas were clearly visible. It was also dividing line between areas of high and low friction. The worn tracks had a rough surface (Figure 2).

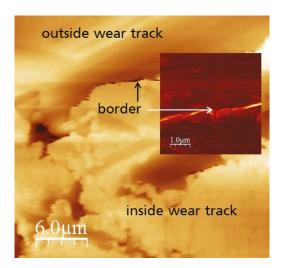


Figure 2. AFM topography and friction images of cast iron disk.

Microtribometer tests were conducted with a reference oil containing the Nanol additive. The results show an instantaneous reduction in the coefficient of friction (Figure 3).

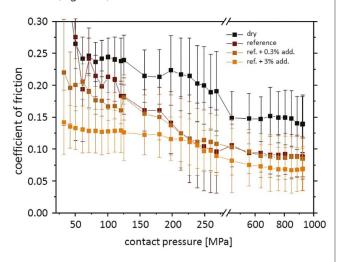


Figure 3. Friction measurements with micro-tribometer.

Sliding friction and wear tests were also carried out, with the additive causing an instant drop in friction and wear (Figure 4).

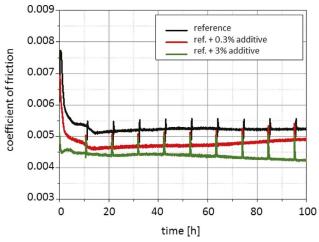


Figure 4. Continuous friction and wear measurement.

In addition, rolling friction and wear tests were conducted in a bearing rig. The results confirm the fast reduction of friction (Figure 5). After this initial reduction, the coefficient of friction is stable on a long-term basis. No signs of wear, cracks, or embrittlement were detected on the bearings (Figure 6).

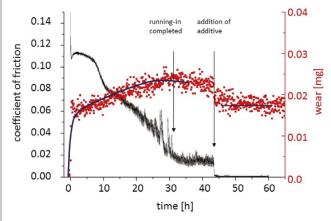


Figure 5. Summary of roller thrust bearing tests.

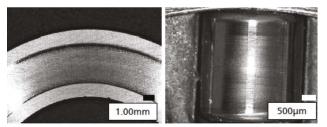


Figure 6. Inspection of roller bearing parts.

The bearing was analysed and copper from the additive was intermixed with the iron lattice, up to a depth of 300 nm.

Pitting test results show that the reference oil without Nano additive produces WEC within 45 hours. With the Nano additive the test reached 422 hours with no formation of WEC. This test result demonstrates that the additive produced a tenfold improvement in WEC lifetime performance.

The results from hydrogen permeation tests (Figure 7) show that the untreated membrane had a much higher saturation concentration with hydrogen. The test with the Nanoadditive had a much lower saturation point. This confirms that the additive reduces the amount of hydrogen that permeates into the steel membrane, and thereby reduce WEC and embrittlement.

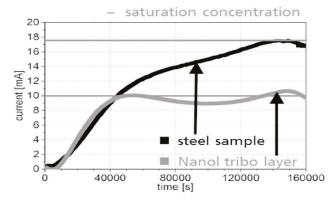


Figure 7. Hydrogen permeation results.

Discussion

The independent testing verifies the Nano additive's performance advantages. It confirms that the additive consists of copper nanoparticles, dispersed in reverse micelles, within a stable colloid, which gives the unique oil solubility properties. It also demonstrates that the nanoparticles give the additive its outstanding performance advantages.

At the recommended treat rate, the additive contributes only a minimal level of sulphated ash to the finished oil. It also contains no sulphur or phosphorus. And enables the formulation of ultra-low phosphorus and potentially zero-phos lubricants.

The Nanoadditive forms very effective tribofilms and this is crucial to friction reduction and wear protection. The mechanism for tribofilm formation consists of a three-phase process (Figure 8).

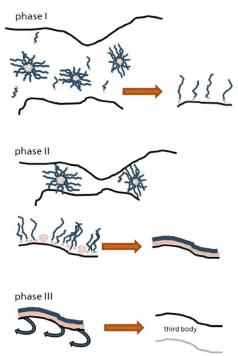


Figure 8. Three Phase Model.

Phase 1: adsorption of copper oleate to the friction surface → instant friction reduction

Phase II: shear-induced disruption of micelles → copper nanoparticles deposit metal surface Copper nanoparticles reorganise to form tribofilm → friction reduction & wear protection

Phase III: Cu²⁺ redox reaction with iron surface to form Cu⁰ → reinforces & sustains tribofilm Copper is key constituent of third body → third body is self-regulating solid lubricant Plastic flow of asperities → mechanical intermixing

Plastic flow of asperities → mechanical intermixing and tribochemical reactions

Copper diffusion into sub-surface → prevents pitting, embrittlement & WEC

In the first stage, the copper oleate, is adsorbed on the friction surface to form a conventional boundary film. This enables an instant reduction in friction.

The second phase is initiated by interactions of the additive with metal asperities on the friction surfaces. It causes the micelles to be disrupted, and release the copper nanoparticles, which deposit on the metal surfaces. They adhere to the surface, and accumulate to form a nanometer-thin metal tribofilm. The film is in dynamic equilibrium, where layers of copper atoms are worn away, but are then quickly replaced, in a self-healing process. This sustains friction and wear performance.

In the third phase, the tribofilm integrates into the structure of the near-surface metal by diffusion. The intermixing produces the "third body", which provides further protection against wear and WEC.

Conclusions

The laboratory tests confirm that the additive delivers excellent long-term friction reduction, wear protection, and prevents WEC. The mechanism and function of copper tribofilms involves a three-phase process. In the first phase there is an instantaneous reduction in the coefficient of friction. The second phase there an even larger decrease in friction, due to the formation of a tribofilm, composed of copper monolayers. In the final step there is mechanical intermixing, leading to the formation of the third body. The copper tribofilm also diffuses into the sub-surface. These processes provide sustained friction reduction and wear protection.

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