Impact of Yttria Reinforced Nanolubricants onto the Tribological Properties

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Abstract: *The continuous improvement of the tribological properties of lubricants is a vital task for engineers, not only in the case of internal combustion engine applications. The researchers are working on investigating different materials to find the possible lubricant additives of the future. One of the possibilities can be the different nanoparticles. Their spherical geometry with nanoscale can provide excellent tribological properties but they must be thoroughly investigated before using them in real machines. This paper introduces the experimental results with spherical yttria nanoparticles as tribological additives in different lubricant types. Ball-on-disc tribometer measurements were carried out to define their frictional behavior and the arisen wear scars were analyzed via high-magnitude scanning electron microscope completed with EDX element analysis. The yttria reinforced nanolubricants have provided astonishing antiwear properties and the SEM images have revealed marks that refer to the mending as their main working mechanism.*

Keywords: *Tribology, yttrium oxide, yttria, nano-ceramic, lubricant, additive, engine*

1. Introduction

Because of the strict emission and fuel consumption regulations all around the world, engine developers have to face huge challenges. To fulfill these regulations the whole vehicle including the combustion powertrain must be further developed to reduce the emission of harmful exhaust gas components, such as CO, NO_x, soot, or unburned fuel particles. The applied lubricants in the internal combustion engines play a crucial role in the tribological processes inside the engine, which also influences the emission and fuel efficiency of the engine. The current lubricants used inside the engines are very complex liquids and they contain different additives to influence the tribological effects of the lubricants and so of the engines as well.

Several research fields are existing to increase the tribological performance of the lubricants and so increase the efficiency of the engines. Low-viscosity lubricants were developed (e.g., SAE 0W-20 viscosity class) to lessen the internal friction of the liquid. Further research activities are running all around the world to find the possible lubricant additives of the future as well. The ionic liquid is a very hopeful field to replace the currently used materials of the engine oils.

Another promising field is the nano-scale particles used as tribological lubricant additives. These materials are scientifically researched in the past 10 years deeply by numerous scientists and they have reported significant improvements used different materials as nano-scale additives. These nanoparticles can be made from metal-oxides (e.g., TiO_2, CuO, Fe_3O_4, ZnO, Co_3O_4, Al_2O_3, etc.), metal-sulfides (MoS_2, WS_2, FeS, etc.), nanocomposites (Cu/CeO_2, Al_2O_3/SiO_2, ZrO_2/SiO_2, etc.) or rare-earth metal compounds ($CeVO_4$, Y_2O_3, $La(OH)_3$, LaF_3, etc.) [1]. The geometry of these nanoparticles can also be different: spherical, granulate, lamina, nanotube, or multilayer [1]. The size of the particles also plays a critical load in the measurable tribological properties of nanoparticles: Peña-Parás et al. have proved in their research that only those particles can provide positive effects whose average particle size is lower than the average roughness (Ra) of the contacting surfaces [2].

Different working mechanisms were reported by Zhang et al. to explain how these nanoparticles can provide such promising tribological properties: rolling (ball bearing), mending, polishing, and protective film mechanism [3]. However, each nanoparticle compound can act differently because of its particle size and hardness, which requires analyzing them with simplified methods before they could be used in a real operating machine.

The tribological properties of nanoscale yttrium oxide (yttria) particles were experimentally analyzed via ball-on-disc simplified tribological measurement method. Nanoscale yttria particles (CAS number: 1314-36-9) were used for these investigation activities with an average particle diameter of less than 50 nm. This paper contains the results and discussion of these experiments.

2. Yttrium oxide nanoparticles

Yttrium oxide (yttria, Y_2O_3) is an air-stable, white, solid crystalline oxide of yttrium transition metal. Yttria closely resembles lanthanide oxides in most of their properties. Generally, yttria is produced by the calcination of yttrium containing compounds and ores like samarskite-(Y) and yttrobetafite-(Y). The other industrial producing possibility is the solvent extraction from ores that also contain the heavier lanthanides. Yttria occurs naturally in its mineral, known as yttrialite-(Y). Naturally, yttria appears with a cubic centered crystalline structure but the structure depends on the temperature. Its body-centered cubic structure (Figure 1.) changes phase to a hexagonal form above 2640 K temperature [4].

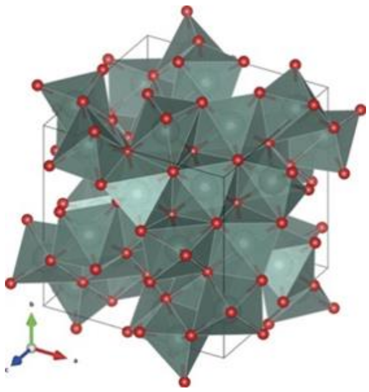

Fig. 1. Body-centered cubic crystal structure of Y_2O_3 [5]

Yttria is mainly characterized by its high thermal stability, and it is suitable for extreme operating conditions. The material engineering applications are based on this property. Due to its rarity, yttrium oxide is rarely used alone, usually as an additive in combination with other substances. Y_2O_3 is used in various applications: stabilizing zirconia against its phase transformation on elevated temperatures; as a sintering aid for silicon nitride and SiAlON ceramics, strengthening nickel alloys, LED components, producing high-temperature resistant transparent ceramics, basis material for solid-state lasers, the raw material for high-temperature superconductors and microwave filters [5].

The density of yttria is around 4.8-5.07 kg/m^3 and its plane strain fracture toughness varies between 1.2 and 3.27 GPa, depending on its production process. Cubic yttria has higher hardness (~2200-2800 HV) compared to steels. The bending strength of yttria (15-140 MPa) varies on a wide scale depending on its temperature, while Young's modulus of yttria (146-168 GPa) is lower than the common steel types [6]. Yttrium oxide is very similar in its properties to lanthanide oxides, which are excellent lapping agents [5]. Due to its physical properties, yttrium oxide can show a lapping-polishing mechanism of action when used as an additive in a tribological system.

Only a limited number of research papers are dealing with the characterization of net yttria ceramic material. Positive oxidation decreasing properties were reported by Wukusick when it was used as an alloying material [7]. In a research paper by Liu et al., the yttria was used as a lubricant additive and they investigated its corrosion preventing properties on the surfaces of specimens from 6061 Al alloy and 304 stainless steel materials with a pin-on-disc tribometer [8]. He et al. investigated sheet-like 2D yttria nanoparticles as liquid additives and they have reported a significant improvement in the mechanical and flow phenomena of various fluids [9].

3. Investigation methods

One of the key elements of the characterization of nanoparticles in liquids is the mixing procedure to homogenize them. No universal homogenization procedure can be found in the literature, so a self-developed mixing procedure were used for this purpose. For the tribological experiments both neat Group III base oil and engine oil with SAE 0W-20 viscosity class were used. The liquids were provided by MOL-LUB Ltd. The yttria particles were doped in the liquids and these mixtures were homogenized with magnetic stirrer for 3 minutes at 100 rpm and with ultrasonic homogenizer for 30 minutes and 50°C. After the ultrasonic homogenization the lubricant samples were further stirred magnetically until the lubrication pipes inside the tribometer were filled up with them.

For the tribological measurements the ball-on-disc system of an SRV®5 type tribometer were used. The specification of the specimens was correlated to the ISO 19291:2016 [10] standard. To simulate the circumstances of the lubricants inside the engine as precise as possible, a method with a self-developed setup parameters were used [11]. This method contains a supplementary oil circuit with a peristaltic pump which realize a continuous oil flow of 225 ml/h to the testing specimens and leads the used lubricant to the pump again. An oscillation movement were realized between the ball and disc specimens with 1 mm stroke, 50 Hz frequency. Both the specimens and the used lubricants were heated up to 100°C temperature separately. A 50 N preload was applied to the ball specimen for 30 seconds to avoid high damages in the specimen surfaces during the run-in phase and a further 2 hours of test with higher normal forces (100 N in case oil base oil, 200 and 300 N in case of formulated engine oil) was carried out to investigate the friction and wear behavior of the lubricant samples. The used testing machine with the realized oil circuit is presented in Fig 2.

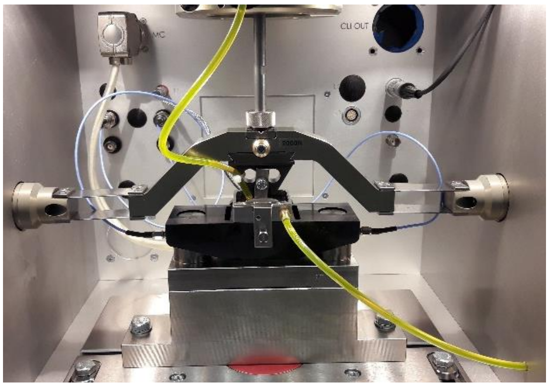

Fig. 2. The used Optimol SRV®5 tribometer with the installed pipes of the oil circuit

For the evaluation of the results, two different friction coefficient values were used, which were recorded with 1-second recording frequency:

- COF (coefficient of friction) value: the maximum friction coefficient value during one stroke, which arises usually from the dead centers of the oscillation movement, representing the property of the system under boundary lubrication conditions.
- FAI (friction absolute integral) value: an average value calculated from the area under the friction coefficient values recorded with high frequency, representing the property of the system under mixed and hydrodynamic lubrication regimes.

The produced wear scars on the ball and disc specimens were analyzed via digital (Keyence VHX-1000) and scanning electron microscope (Hirox SEM 4000M). The main goal of the microscopic investigation is to investigate the wear behavior of the yttria-doped lubricant samples. The wear scar diameter (WSD) on the ball specimens was measured in the direction of parallel and perpendicular and their average value was used for further evaluation. High-resolution SEM images were taken to analyze the possible yttria distribution on the worn surfaces and to define the major wear patterns on the surfaces.

4. Experimental results and discussion

The characterization of the yttria nanoparticles should have started with the investigation of dispersant necessity for the nanoparticles. As a dispersant, we used Triton X-100, because its chemical properties are the best to provide homogeneous nanoparticle distribution. Four different lubricant samples were prepared: neat Group III base oil as the reference, Gr III doped with 0.5% yttria nanoparticles, Gr III with 1 wt% of TX100, and Gr III doped with both 1 wt% TX100 and 0.5 wt% Y_2O_3. The results of the tribometer measurements are illustrated in Fig. 3. The bar chart clearly illustrates the trend, that the yttria-doped lubricant without dispersant provides no positive tribological properties, but in the case of the triton-doped samples, the positive effect of the yttria nanoparticles is significant. According to these results, only TX100-doped lubricant samples were used for further investigations.

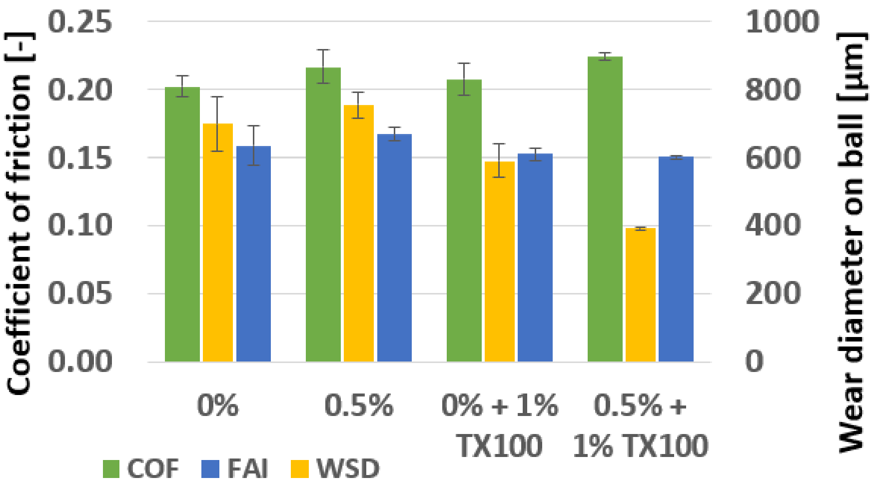

Fig. 3. Comparison of the tribological results with triton-doped and non-triton doped oil samples

To investigate the optimal yttria concentration in the lubricants, samples with 6 different concentrations were prepared (between 0.1 and 0.6 wt%). The tribological properties of these samples were tested with the same tribometer method and the results were presented in Fig. 4. It can be clearly seen that an optimum can be observed at 0.5 wt%: the measured wear scar diameter has significantly reduced with only a small amount of friction increase. The 0.4 wt% concentration has also shown an interesting tendency: the friction coefficient was reduced slightly, but the WSD on the ball specimen has increased and the measurable deviation has been also raised.

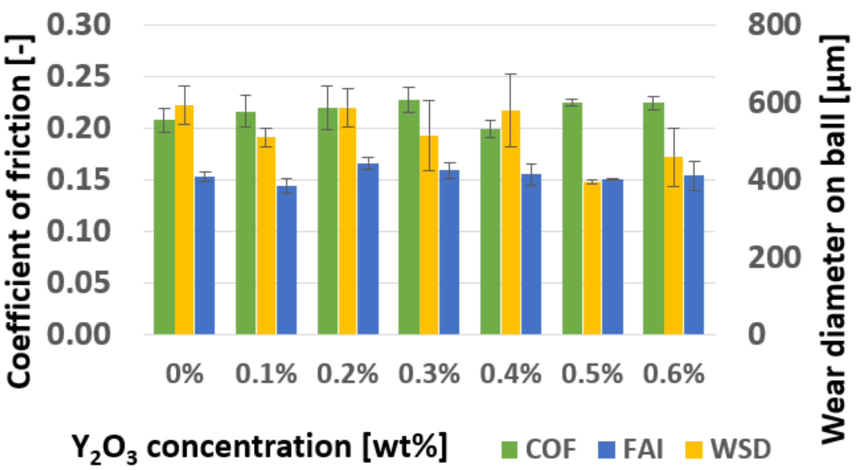

Fig. 4. Comparison of the experimental results of analyzed Gr III-based lubricant samples with various nanoparticle concentration

Similar yttria concentrations were also prepared based on the 0W-20 engine oils including 1 wt% of TX100. The tribological measurements with the same evaluations were carried out under two normal load values, 200 N and 300 N. The evaluation of the tribological results is presented in Fig. 5. The bar charts clearly illustrate the optimum concentration of yttria nanoparticles: 0.1 wt% yttria under 200 N and 0.2 wt% of yttria under 300 N load. Under both normal forces, the friction coefficient and the wear scar diameter were also reduced significantly.

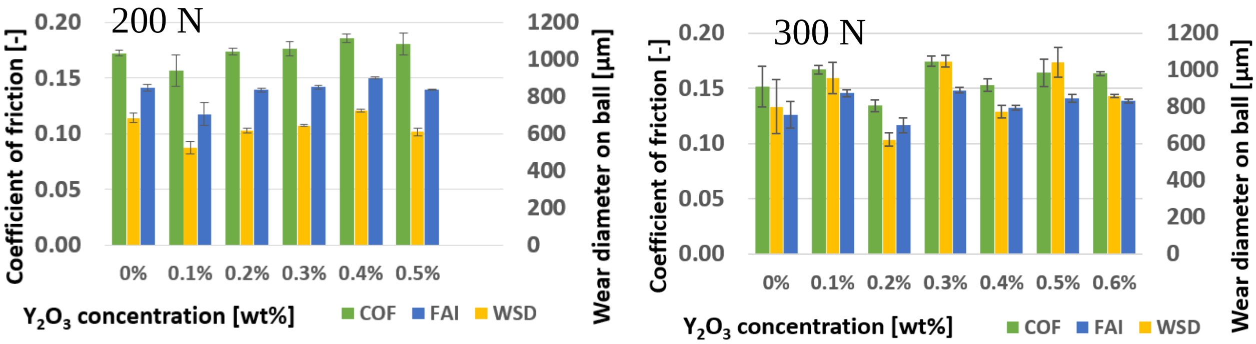

Fig. 5. Comparison of the experimental results of analyzed 0W-20-based lubricant samples with various nanoparticle concentration under 200 N (left) and 300 N (right) load

The digital microscopic analysis of the ball specimens has revealed an astonishing wear reduction property of the yttria nanoparticles. The wear scars on the disc specimens were also analyzed to understand how the wear was produced. The digital microscope images can be observed in Fig. 6. It can be stated that in the case of 100 N and 200 N loads the wear depth is enough low to see the valleys of the surface roughness. Besides, a significant positive effect of the yttria particles can be defined according to the images.

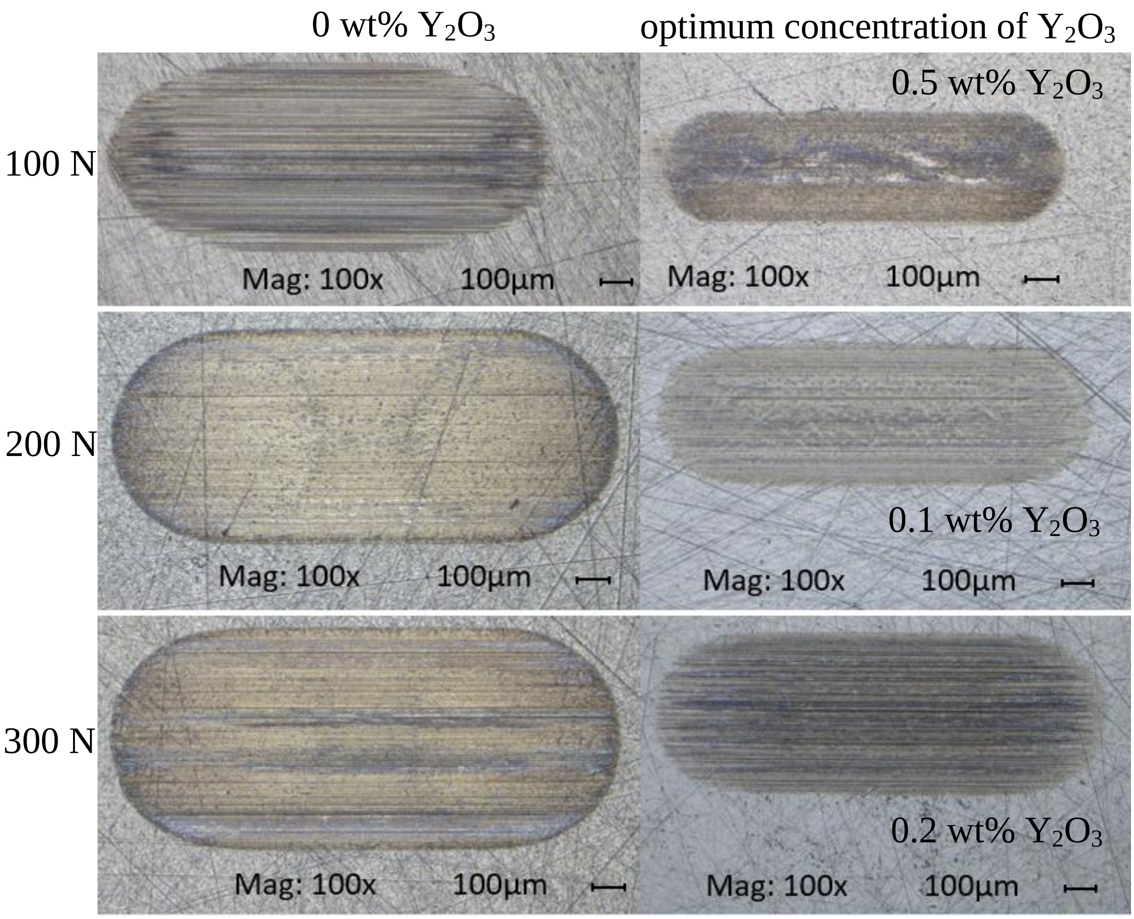

Fig. 6. Comparison of the wear scars on the disc specimen using digital microscopic images

Further scanning electron microscopic analysis was also carried out to define the wear mechanisms and the existence of yttria nanoparticles on the worn surface. Fig. 7. illustrates the SEM-images mage on the worn surface of the disc specimens with 0.5 wt% Y_2O_3 and 1 wt% TX100-doped Gr III base oil. The wear scars on the images can barely see and the grooves of the original surfaces are also seeable which proves the excellent antiwear properties of the investigated yttria nanoparticles. The EDX-analysis reveals that the yttria nanoparticles are collected in the grooves and on the top layer of the surface too. These SEM results are proof that the yttria nanoparticles are working by the mending mechanism.

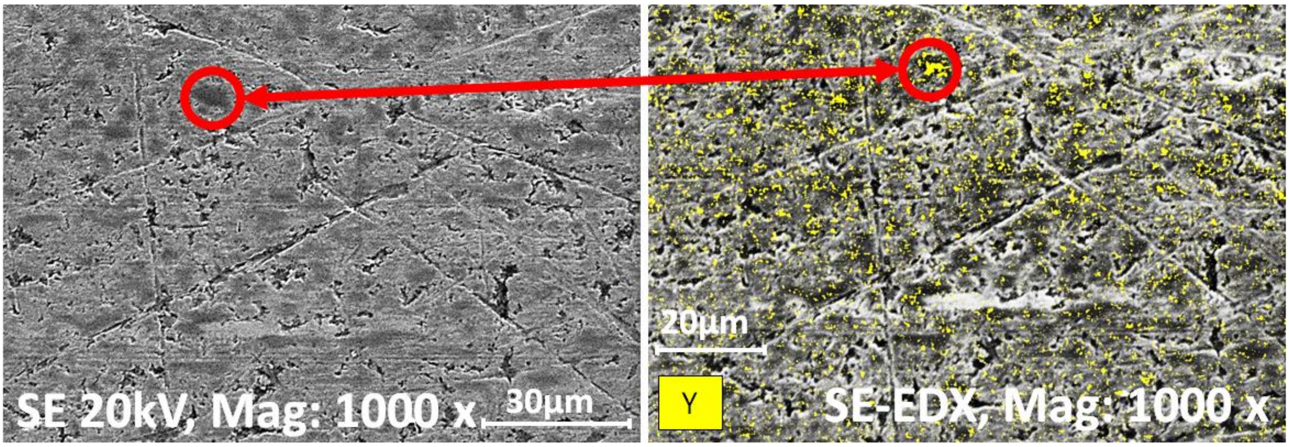

Fig. 7. SE-Scanning Electron Microscope image and EDX mapping picture about the surface of disc specimen with 0.5 wt% Y_2O_3 doped Gr III base oil

The element distribution on the worn surface was also investigated with the EDX sensor or the used scanning electron microscope. The worn surfaces with both the reference oil sample (Gr III base oil + 1 wt% TX100) and the optimum sample (Gr III base oil + 1 wt% TX100 + 0.5 wt% Y_2O_3) were quantitatively analyzed to understand how the tribosystem has changed with the addition of yttria nanoparticles. The measured data can be observed in Table 1. The results show a significant increase of yttrium, oxygen, and carbon elements on the worn surface with yttria-doped samples. The increased amount of carbon element can be explained by the increased amount of base oil molecules attached to the worn surface, compared with the yttria-free sample. The reference sample showed a high amount of wear which has reduced the amount of adhered base oil molecules to the surface, and this process did not appear in the case of yttria-doped samples. The significant increase of yttrium represents the number of yttria nanoparticles on the surface. The oxygen increase can indicate two effects: the presence of yttria nanoparticles on the surface and a small amount of oxidation of the metal substrate. For the SEM images, the specimens were thoroughly cleaned in an ultrasonic cleaner with brake cleaner liquid and at a temperature of 50°C multiple times, and the nanoscale yttria particles could be observed even after his cleaning procedure. The particles in this scale level can adhere to the surfaces via van-der-Waals forces, which can explain how the yttria nanoparticles worked on the surface and how they could realize their astonishing antiwear properties.

Table 1: Quantitative element analysis (wt%) on the worn surface of the disc specimen with 0.5 wt% Y_2O_3 lubricant sample and comparison with the reference results

Element	Gr III + 1% TX100	Gr III + 1% TX100 + 0.5% Y_2O_3
Fe	95.92%	77.43%
Cr	1.34%	1.24%
Si	0.11%	1.9%
O	1.52%	9.54%
C	1.11%	8.11%
Y	0%	1.78%

Compared to the previous results with the same investigation methods with Group III-based oil samples [12, 13], the yttria nanoparticles have provided astonishing antiwear properties and the measurable friction coefficient values could be reduced in case of the engine oil investigations too. The yttria nanoparticles could also fill up the surface roughness valleys and wear grooves, similar to the previously investigated zirconia nano additives [12]. However, the purchase costs of the yttria nanoparticles are significantly higher compared to the zirconia ones. The tribological investigation of the so-called yttria-stabilized-zirconia (YZS) [14] can be interesting, which could provide the excellent antiwear properties of the yttria nanoparticles cost-effectively.

5. Conclusions

This paper presents the results of the experiments with spherical yttria nanoparticles homogenized into a neat Group II base oil and a fully formulated engine oil with the viscosity class of SAE 0W-20. For the investigations, a ball-on-disc tribosystem completed with a wide microscopic analysis was carried out.

As the result, the following statements can be formulated:

- To achieve the maximum potential inside the yttria nanoparticles, an extra dispersant additive (Triton X-100) had to be mixed into the yttria-doped lubricant samples.

- The yttria nanoparticles have provided excellent antiwear properties for the used lubricants. The reduction of the wear scar diameter on the ball specimens was measured as 33% in Group III oil, 23% in engine oil under 200 N, and 22% under 300 N. In most of the cases, the measured friction coefficient values were also reduced.

- Different optimum concentrations could be defined, and their value was highly dependent on the used basis liquid. 0.5 wt%, 0.1 wt%, and 0.2 wt% values were determined in the case of neat Group III base oil, engine oil under 200 N, and engine oil under 300 N, respectively.

- The working mechanism of the yttria nanoparticles was examined with a scanning electron microscope completed with an EDX element analysis. According to the observed SEM-images it can be stated that the yttria nanoparticles could attach to the contacting surfaces via van-der-Waals forces, fill up the wear grooves and roughness valleys resulting in a smoother contact surface. This mechanism explains the excellent antiwear properties of the yttria nanolubricant.

The yttria-doped nanolubricant samples have provided astonishing antiwear properties to the investigated ball-on-disc tribosystem in both neat base oil and fully formulated engine oil. The purchase costs of the yttria nanoparticles lessen its potential to use in the engines of passenger cars in the future as well. To reduce the costs, tribological analysis of additional nanoparticles is recommended (e.g., yttria-stabilized-zirconia). Further investigation methods are also recommended to analyze the impact of nano additives for the engines like fuel- and oil consumption or exhaust gas emission.

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