engineering proceedings

MDPI

Proceeding Paper

Investigation of the Effects of CuO Nanoparticles on the Tribological Properties of Thermally Aged Group III Base Oil †

Ádám István Szabó * and Péter Bence Pápai

Department of Propulsion Technology, Széchenyi István University, Egyetem tér 1, H-9026 Győr, Hungary
* Correspondence: szabo.adam@sze.hu
† Presented at the Sustainable Mobility and Transportation Symposium 2024, Győr, Hungary, 14–16 October 2024.

Abstract: Protecting our environment is a primary focus in various industries, including the automotive sector, which aims to reduce friction and wear to minimize emissions. This study examines the effect of cupric oxide nanoparticles on artificially aged Group III base oil under lab conditions. The oil, aged using a temperature-focused method, was homogenized with 0.5 wt% cupric oxide nanoparticles. A ball-on-disc tribological system registered static and hydrodynamic friction. Wear track sizes indicated the nanoadditive's positive impact compared to the oil without additives. The experiments revealed the anti-aging effect of cupric oxide nanoceramics. Lubricant aged with cupric oxide performed similarly to new oil, and cupric oxide nanoparticles positively affected friction and wear. The oil supplemented before aging showed better tribological results than after aging.

Keywords: nanoparticles; oil aging; tribology; lubricant; cupric oxide; friction; wear

1. Introduction

For continuous improvement, it is essential to enhance the efficiency of existing machines alongside adopting new technologies. By reducing the internal friction of internal combustion engines in passenger cars, we can achieve lower fuel consumption and reduce harmful emissions. Using nanoceramic additives in lubricating oil can be a solution to reduce friction. Since the working conditions of lubricants are affected by aging during the oil change period, it is crucial to examine the behavior of nanoadditives during aging. This study focuses on the thermal artificial aging of Group III base oil using cupric oxide (CuO) nanoadditives. Nanoadditives improve the lubricating properties of oil and can fill in grooves caused by surface roughness [1,2] and cover the surface with an elemental copper layer through triboreduction [3]. These properties can lead to machines operating more efficiently due to reduced friction. Alongside its favorable properties, CuO nanoparticles should be used cautiously, considering their effects on the environment and living organisms. In plants, CuO nanoparticles cause abnormalities in growth, and in living organisms, they can damage cell walls [4].

Many researchers use artificial oil aging to simulate the months-long processes occurring in an internal combustion engine within a shorter period. This study adopts the aging method developed by Besser et al. [5], aiming to reproduce the engine oil used in real internal combustion engine cars under laboratory conditions. One primary goal of their experiment was to produce aged oil in large quantities. They compared two methods using two commercially available engine oils. A significant difference between the methods was the quantity of aged oil produced. Small batch experiments used 300 g of oil with only air passed through a three-neck flask. In contrast, extensive batch experiments used a 250 L tank with 100 L of oil, continuously mixed with an external mixer in addition to gas introduction. In both cases, the temperature was maintained at 180 °C. The results indicated that mixing facilitated oxidation in the aged samples.

check for updates

Citation: Szabó, Á.I.; Pápai, P.B. Investigation of the Effects of CuO Nanoparticles on the Tribological Properties of Thermally Aged Group III Base Oil. *Eng. Proc.* **2024**, *79*, 82. https://doi.org/10.3390/engproc2024079082

Academic Editors: András Lajos Nagy, Boglárka Eisinger Balassa, László Lendvai and Szabolcs Kocsis-Szürke

Published: 12 November 2024

Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

A simplified method was applied, focusing solely on the effect of heat while maintaining mixing with a magnetic stirrer. Aging with gas introduction better reflects real-life conditions [6], but this would result in such significant aging in Group III base oil that it would not yield valuable tribological results. Formulated oils contain additives that inhibit aging and oxidation, making them much more resistant and unsuitable for direct comparison with the base oils used in experiments. Besser's simultaneous thermal oxidation experiments used condensate for further analysis, but condensate decreases at lower temperatures, making it unfeasible to examine. Hence, condensate separation was not continued [7]. In exploring the potential of nanoadditives, it is crucial to test them in various environments, including artificially aged oil.

This article's novelty lies in the development and execution of a series of experiments that include aged and nanoadditive samples. It aims to explore an area with limited available information.

2. Materials and Methods

The tests were conducted on Group III type base oil with a viscosity of 4 cSt, provided by MOL-LUB Kft (Almásfüzítő, Hungary). Five samples were used during the measurements, including artificially aged samples under laboratory conditions and fresh reference samples. The reference value was the new Group III (G3) without additives. An additive-free aged sample (AG3) and a sample with additives without aging (G3+CuO) were prepared, as well as two aged samples with CuO added after aging (AG3+CuO) and before aging (CuOAG3). The difference between the two additive-containing samples was the timing of the additive addition.

The experiments used surface-activated cupric oxide (CuO, CAS 1317-38-0) nanoceramics with a 30–50 nm particle diameter range. The additive was surface activated with ethyl oleate to ensure a more homogeneous mixture and minimize aggregation [8]. The surface-activated CuO nanoadditive was mixed into Group III base oil at a concentration of 0.5 wt%, supplemented with toluene as a dispersing agent, which was evaporated from the oil sample after 16 h of continuous mixing. Before use, the oil sample was homogenized for 15 min at 50 °C using an ultrasonic mixer.

The artificially aged samples were prepared using a Faithful 98-III-B magnetic stirrer-equipped flask heater. A mild heat treatment-like aging process was chosen to reproduce the beginning phase of the base lubricant aging. The aging process was performed at 140 °C temperature for 24 h. An amount of 75 g of Group III oil was aged in a 300 mL round-bottom flask, sealed with a rubber stopper suitable for the neck diameter to ensure proper sealing throughout the aging process. The oil sample reached 140 °C in 25 min when the 24 h aging period began. Stirring was activated from the start of heating and continued throughout the entire process. Stirring is crucial to ensure the oil's homogeneity during aging, as the nanoadditive tends to settle without mixing. All oil samples for the measurements were aged in this manner. This simplified method is suitable for detecting the effects of mild or initial oil aging. Much more aging could be achieved with extended aging periods, higher temperatures, or adding extra oxygen.

Viscosity measurements and Fourier-transform infrared spectroscopy (FT-IR) analyses were performed on all used oil samples. Viscosity was measured using an Anton Paar SVM 3001 machine in the temperature range of 40 °C to 120 °C with 10 °C increments according to ASTM D7042 standard [9]. FT-IR analyses were conducted on a Bruker INVENIO-S device using a KBr (potassium bromide) cuvette.

The tribological measurements were conducted using an Optimol SRV®5 tribometer. A standard DIN 100Cr6 material grade ball-disc tribo system was used during the measurements, and the worn specimens were analyzed according to the ISO 19291:2016 standard [10]. The tests involved an oscillating motion with a stroke length of 1 mm over 7230 s. A load of 50 N was applied to the tribo system through a push rod for the entire test duration. At the end of the measurement, the contact pressure was 210–500 MPa, depending on the tested oil sample. The test specimens and the circulating oil temperature were

maintained at 100 °C. The tribometer examines two characteristic friction values: static friction (COF) at the stroke dead points and dynamic friction (friction absolute integral method—FAI) with high-speed data collection (25 kHz). FAI is a value that refers to the entire stroke.

After conducting tribological measurements, multiple microscopic examinations were carried out on the worn surfaces of the test specimens. To determine the wear scar diameter (WSD) on the ball specimens, a Keyence VHX-1000 digital microscope was used at 200× magnification (see Figure 1 left and middle). In addition to the digital microscope images, a Leica DCM3D confocal microscope was employed (Figure 1 right). This instrument allows for the determination of wear depth and profile, and the Leica Map software facilitates the calculation of wear volume (WV) from the obtained data.

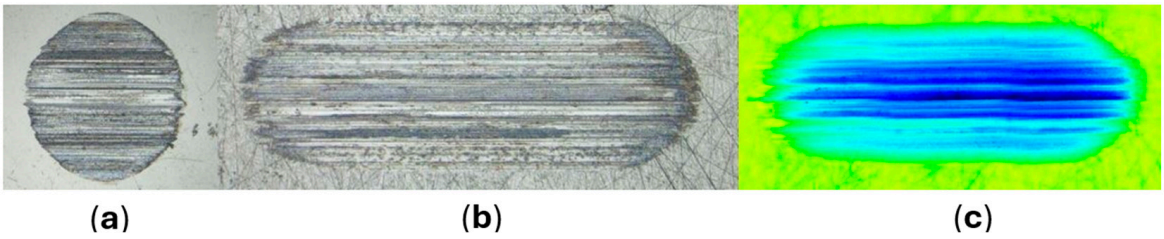

Figure 1. Wear scar on the ball (**a**) and wear on the disc (**b**) under the Keyence VHX-1000 digital microscope, supplemented with a false-color height image of the disc wear (**c**) taken with the Leica DCM3D confocal microscope.

3. Experimental Results

During the FT-IR analysis of the oils, it was observed that heating induced oxidation in the aged oil samples, which was consistent with expectations (see Figure 2). Throughout the aging process, the oxygen content in the air remaining in the flask oxidizes the oil sample, which is evident in the wavelength region around 1720 cm^{-1}. Furthermore, FT-IR detected the presence of CuO in the respective lubricating oil samples, specifically in the ~546 cm^{-1} region. The group of hydrocarbons can be observed in the 2800–3000 cm^{-1} range.

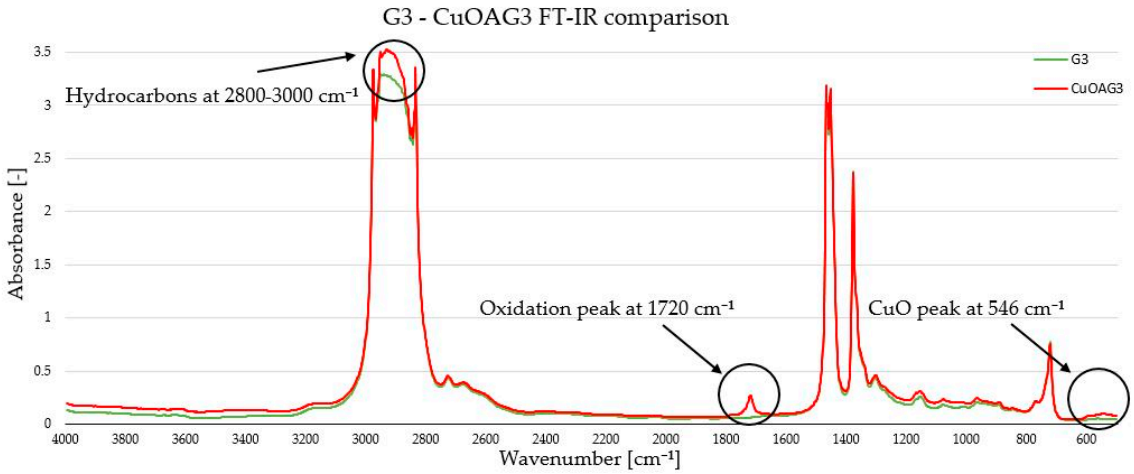

Figure 2. Comparison of FT-IR spectra of Group III base oil and CuO-aged Group III oil samples.

Since no external air was introduced into the flask during aging, the extent of aging primarily resulted from the air trapped inside the flask and thermal aging effects. Another indicator of aging severity is the change in kinematic viscosity, which can increase by as much as 11% at low temperatures (40 °C). During the examination of kinematic viscosity (see Figure 3), it can be determined that the viscosity of all oil samples increased compared to the reference oil (G3). Both aging and the addition of nanoparticles increase the viscosity

of the lubricant. It can be established that CuO nanoparticles slow down the aging of the lubricant oil (anti-aging), as the kinematic viscosity of the oil sample aged without the CuO additive (AG3 40 °C: 21.2 cSt) is higher than that of the sample aged with CuO nanoadditives (CuOAG3 40 °C: 20.7 cSt). The highest viscosity is observed when an aged base oil is supplemented with CuO nanoparticles (AG3+CuO 40 °C: 22.0 cSt). These trends are consistent across the entire range. The viscosity difference between the lubricants is most significant in the lower temperature range (<60 °C), where up to a 10% difference can be observed between the samples. The relative viscosity difference between the oil samples decreases at higher temperature ranges. At the 100 °C temperature used in tribometer measurements, the differences are within 3.4%, which has a minor influence on the final results of the friction measurements.

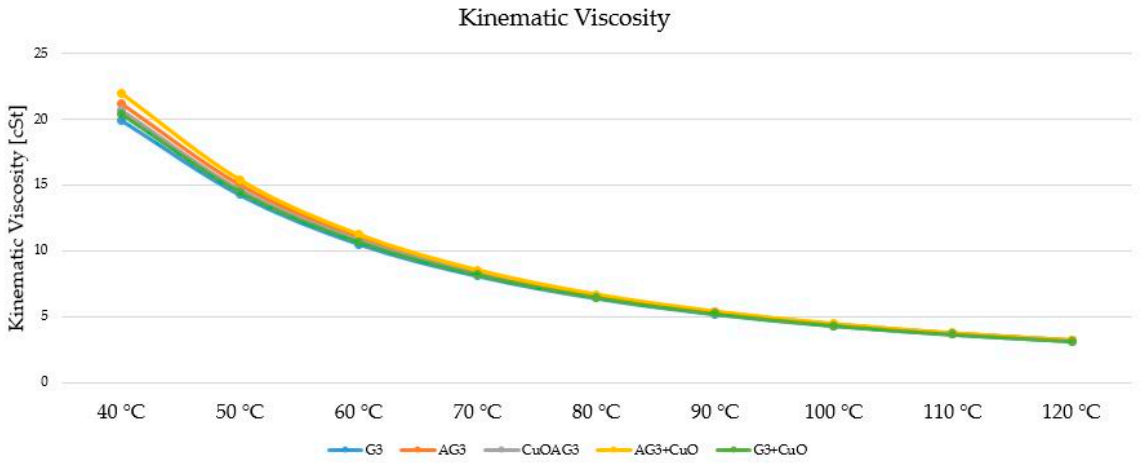

Figure 3. Comparison of kinematic viscosity among the examined oil samples.

The authors have previously demonstrated the excellent friction-reducing properties of CuO nanoparticles during triboreduction in their earlier research [8]. Upon examining the friction results, it can be concluded that the static friction (COF) and the friction absolute integral (FAI) show consistent trends when comparing the oil samples (see both in Figure 4). It was found that both aging and CuO nanoparticles improved the friction properties of the unaged Group III base oil. Due to aging (AG3), both friction values decreased by 29%, likely due to the formation of tribofilms from oxidation products generated during aging, increased oil viscosity, and improved thermal stability. All oil samples containing CuO nanoparticles significantly reduced friction. With CuO nanoparticles, the static friction decreased by 34–37%, while the friction absolute integral decreased by 35–37%. There is no clear correlation in the lubricating oil samples containing CuO friction results. It can be stated that the friction results of an unaged Group III oil sample with CuO additives can also be achieved by adding the nanoadditive to the aged base oil. The anti-aging property of CuO nanoparticles is also demonstrated by the fact that after the aging procedure, they achieved the same friction values as when new.

Examining the wear scar diameter (WSD) results on the ball test specimens (see Figure 5), it can be determined that while all oil samples improved upon the unaged Group III base oil reference results, certain conclusions can be made. The sample without aging but with CuO additives showed the best result, reducing the wear diameter by 35%. In contrast, aging had a negative effect on wear, although it was still favorable compared to the reference. A significant difference is observed between adding the additive before aging (CuOAG3 WSD: −34%) and after aging (AG3+CuO WSD: −20%). The oil sample aged with CuO nanoparticles showed almost the same result as the new sample, further proving its anti-aging effect.

A similar trend was observed while measuring wear volumes (WV) on the disc but with more considerable differences (see Figure 6). Regarding the WV results, the unaged G3+CuO sample also showed the best performance, reducing wear by 77%. It can also

be noted that mild aging of the Group III base oil (AG3) is somewhat favorable against wear (−38%). Still, the lubricant became unstable due to aging, with a drastic increase in deviation of values. Even adding nanoparticles afterward (AG3+CuO) did not significantly improve the situation. In contrast, the Group III base oil aged with CuO nanoadditives approached values comparable to the new ones (CuOAG3 WV: −69%) with low deviation.

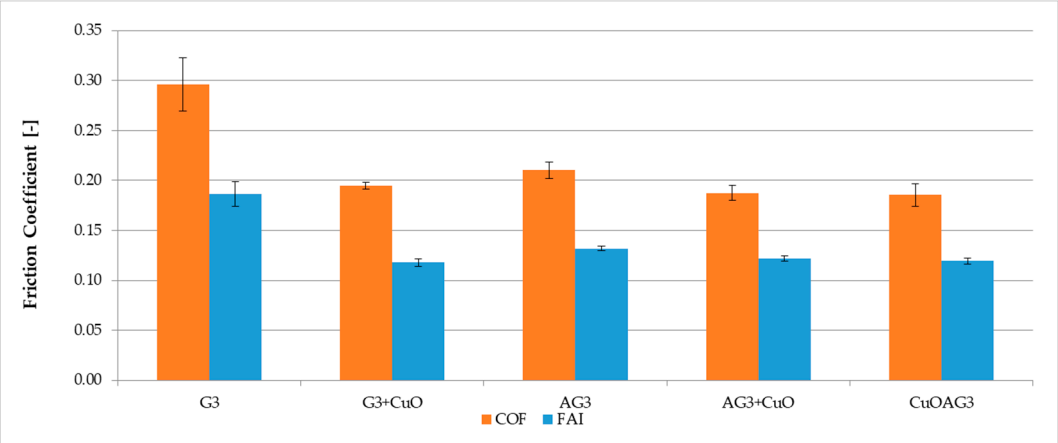

Figure 4. Comparison of static friction (COF) and dynamic friction (FAI) results among the examined oil samples.

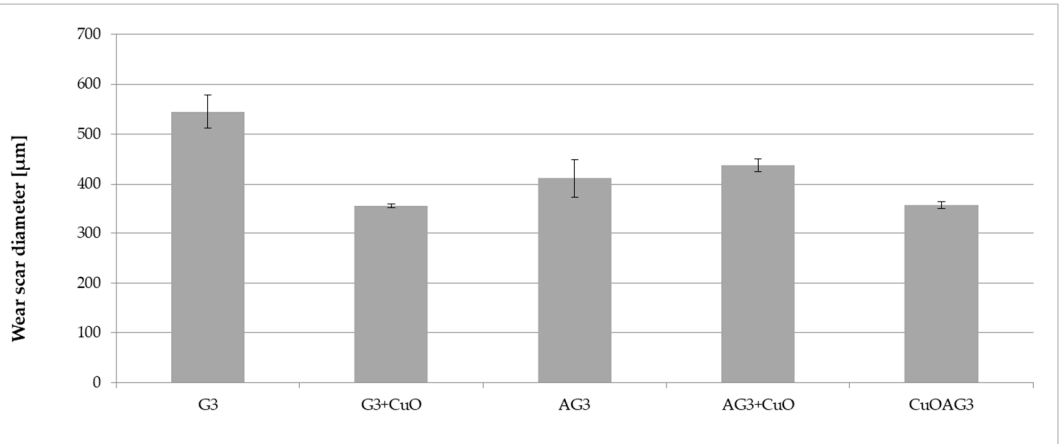

Figure 5. Comparison of wear scar diameter (WSD) results on the balls among the examined oil samples.

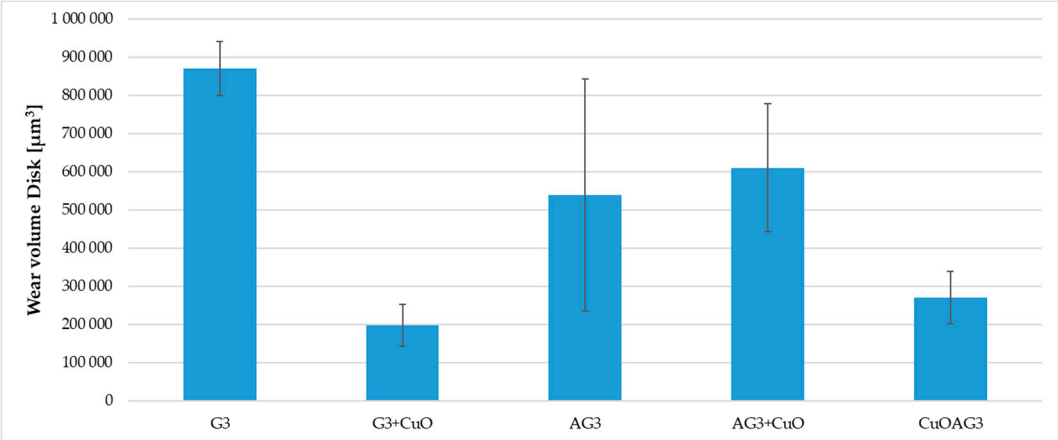

Figure 6. Comparison of wear volume (WV) results on the discs among the examined oil samples.

The anti-aging effect of CuO nanoparticles against thermal aging has been demonstrated. In the future, it would be beneficial to examine the thermal properties of lubricating oils prepared in this manner and the worn surfaces to uncover the underlying processes.

4. Conclusions

The article examined the effects of CuO nanoparticles on the aging of Group III base oil and its tribological impacts. The following conclusions can be made:

- The closed system created with a flask heater produced an artificially aged lubricant that performed tribologically better (both in friction and wear) than the fresh one. These results are controversial and contrary to the known mechanisms and observations from the available literature. These phenomena need to be investigated in detail, and further experiments should be performed to verify the aging effect over extended periods;
- The nanoparticle content of the oil samples and their minor oxidative aging were verified using FT-IR spectroscopy. The kinematic viscosity of the lubricant samples increases with the addition of nanoparticles and aging, particularly below 60 °C. Oil samples show a kinematic viscosity difference within 3.4% at the measurement temperature of 100 °C;
- The thermal aging inhibitory effect of ethyl oleate surface-activated CuO nanoparticles has been demonstrated. CuO prevented increased kinematic viscosity of the lubricating oil during thermal aging. CuO nanoparticles showed excellent effects on a tribological system, capable of reducing both friction and wear. CuO nanoparticles can protect the lubricating oil from thermal aging without significantly compromising friction and wear results compared to new lubricating oil.

Author Contributions: Conceptualization, P.B.P. and Á.I.S.; methodology, P.B.P.; formal analysis, Á.I.S. and P.B.P.; investigation, P.B.P.; data curation, P.B.P.; writing–original draft preparation, P.B.P.; writing–review and editing, Á.I.S.; supervision, Á.I.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This article is published in the framework of the project "Synthetic fuels production and validation in cooperation between industry and university", project number "ÉZFF/956/2022-ITM_SZERZ".

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Chen, Y.; Renner, P.; Liang, H. Dispersion of Nanoparticles in Lubricating Oil: A Critical Review. *Lubricants* **2019**, *7*, 7. [CrossRef]
2. Lee, K.; Hwang, Y.; Cheong, S.; Choi, Y.; Kwon, L.; Lee, J.; Kim, S.H. Understanding the Role of Nanoparticles in Nano-oil Lubrication. *Tribol. Lett.* **2009**, *35*, 127–131. [CrossRef]
3. Tóth, Á.D.; Szabó, Á.I.; Kuti, R.; Rohde-Brandenburger, J. Tribological Investigation of Applicability of Nano-Sized Cupric Oxide (CuO) Ceramic Material in Automotive Vehicles. *FME Trans.* **2021**, *49*, 335–343. [CrossRef]
4. Hou, J.; Wang, X.; Hayat, T.; Wang, X. Ecotoxicological effects and mechanism of CuO nanoparticles to individual organisms. *Environ. Pollut.* **2017**, *221*, 209–217. [CrossRef] [PubMed]
5. Besser, C.; Agocs, A.; Ronai, B.; Ristic, A.; Repka, M.; Jankes, E.; McAleese, C.; Dörr, N. Generation of engine oils with defined degree of degradation by means of a large scale artificial alteration method. *Tribol. Int.* **2019**, *132*, 39–49. [CrossRef]
6. Nagy, A.L.; Rohde-Brandenburger, J.; Zsoldos, I. Artificial Aging Experiments of Neat and Contaminated Engine Oil Samples. *Lubricants* **2021**, *9*, 63. [CrossRef]
7. Besser, C.; Schneidhofer, C.; Dörr, N.; Novotny-Farkas, F.; Allmaier, G. Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component. *Tribol. Int.* **2012**, *46*, 174–182. [CrossRef]

8. Tóth, Á.D.; Mike-Kaszás, N.; Bartus, G.; Hargitai, H.; Szabó, Á.I. Surface Modification of Silica Nanoparticles with Ethyl Oleate for the Purpose of Stabilizing Nanolubricants Used for Tribological Tests. *Ceramics* **2023**, *6*, 980–993. [CrossRef]
9. *ASTM D7042-21*; Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity). ASTM International: West Conshohocken, PA, USA, 2021.
10. *ISO 19291:2016(E)*; Lubricants – Determination of Tribological Quantities for Oils and Greases—Tribological Test in the Translator Oscillation Apparatus. International Organization for Standardization: Geneva, Switzerland, 2016.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.