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RHEOLOGICAL CHARACTERIZATION OF MINERAL OILS WITH ADDITIVES

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Abstract: *Viscosity index improvers moderate the sensitivity of lubricant viscosity to the temperature changes. This study explores the influence of various concentrations of the additive of this type Polybutene 30 (PIB30)to mineral base oil AN46, by using a cone-plate rotational viscometer to assess rheological characteristics at medium to high shear rates. Results indicate typical non-Newtonian properties of the samples, i.e. pseudoplastic fluid behavior, with increasing shear rate leading to heightened shear stress and reduced viscosity. Concentration-dependent trends reveal an association between additive concentration, increased viscosity and shear stress. The investigated lubricants exhibit typical thixotropic properties.*

Key words: *tribology, lubricating oils, additives, viscosity, rheology, cone-plane test.*

1. INTRODUCTION

Enhancing the durability and reliability of tribological units involves minimizing friction losses and reducing wear in machine components. Proper lubrication is essential for normal machine operation, aligning with operating modes, parameters, and appropriate material choices for contact surfaces. The selection of a suitable lubricant tailored to the specific application plays a crucial role in mitigating friction and wear.

As machines evolve with increased velocities, pressures, and loads, there is a simultaneous need to improve lubricant properties and their selection [1]. Various types of additives are commonly introduced to enhance lubricant characteristics across different oil types. For instance, to achieve optimal viscosity-temperature properties, base oils are often blended with viscosity index improvers, such as polyisobutylene [2-6].

In the context of mineral oils incorporating viscosity index improvers, which are polymers with long chains and high molecular weight, the resulting lubricating fluids exhibit non-Newtonian properties. The current study treats a fluid of a similar type and the aim of the investigation is to analyze how the shear rate range and different concentrations of the viscosity index improver affect the rheological characteristics of mineral oil (AN46) with such kind of additives (PIB30).

The investigation took place in a specialized laboratory on rheology equipped with state-of-the-art scientific instruments. The outcomes of the study are graphically visualized, showcasing the relationships between shear stress and shear rate, as well as the correlation between viscosity and shear rate. Additionally, the influence of additive concentration on viscosity is shown, providing a better understanding of the experimental results.

The findings from this study can serve as valuable input parameters in the modeling and simulation of lubrication processes for diverse tribological contacts within the field of scientific research.

2. BACKGROUND

Lubricating oils in a current time are intricate chemical products, whether in their pure form or as a result of blending various base oils (oil base components) with a diverse array of organic and inorganic compounds known as additives [1, 7-

8]. These base oils are categorized as mineral, synthetic, semi-synthetic and biodegradable. Additives are routinely incorporated into the base oil composition to enhance the efficiency of the oils and modify their properties [1, 5-6, 7-9]. The quantity and types of additives in the total oil volume can vary from a few hundredths of a percent to 30 % or more [10, 11].

Various types of additives play distinct roles in lubricating oils. These include extreme viscosity index (VI) improvers, antiwear additives, extreme pressure additives, antioxidants, corrosion inhibitors, detergents and dispersants, depresators, antifoam additives (defoamants), and more, each serving specific functions within the oil formulation.

As widely recognized, the viscosity of oil, serving as a measure of the fluid's internal friction, stands as a pivotal determinant for the lubricants' quality and effectiveness. It exerts a substantial influence on the performance of lubricated contacts within tribological units [6, 12, 13] and is intricately connected to factors such as pressure, temperature, shear rate, etc.

Viscosity index improvers are introduced to decrease the effect of temperature variations on oil viscosity. The viscosity index (VI) is a dimensionless parameter measured on a standardized scale, signifying the oil's viscosity alteration in response to temperature change. A higher VI indicates minimal viscosity change with temperature variations, whereas a lower VI signifies the opposite trend [12-14].

The incorporation of additives like viscosity index improvers (VI improvers) in mineral-based lubricating oils induces non-Newtonian behavior in the fluids. Consequently, there is a specific focus on investigating the rheological properties of these lubricating fluids due to their altered characteristics.

As indicated in [12-13, 15-16] the non-Newtonian lubricants are commonly categorized into plastic, pseudoplastic, and dilatant types. The viscosity of these fluids is occasionally referred to as apparent or initial, recognizing that its values may undergo changes during the lubrication process.

Plastic fluids exhibit solid-like behavior under static conditions; however, under specific circumstances, they transition to a flowing state characterized by a "yield stress." Beyond this threshold, plastic fluids may display Newtonian, dilatant, or pseudoplastic fluid characteristics. A Bingham plastic mass can be considered like a representative example of a lubricant. Pseudoplastic fluids, also known for their "shear-thinning" behavior, experience a reduction in viscosity with an increasing shear rate. Conversely, dilatant fluids, exhibiting "shear-thickening" flow behavior, demonstrate an increase in viscosity with a rise in shear rate. The fundamental rheological characteristics, depicting the dependencies of viscosity and shear stress on shear rate for pseudoplastic and dilatant fluids, can found in [6, 12-13, 15-20].

Just like other varieties of non-Newtonian fluids, the mentioned 3 types are presented by different rheological models. The Bingham model is related to plastic fluids, while the power-law model and the cubic stress model (Rabinowitsch) are utilized to characterize both pseudoplastic and dilatant lubricants. These rheological models provide a framework for understanding and predicting the flow behavior of these diverse non-Newtonian fluids.

Another crucial rheological characteristic involves the influence of time on viscosity values, leading to the classification of non-Newtonian fluids into two distinct behaviours. Thixotropy is characterized by a decrease in viscosity over time when subjected to a constant shear rate. In contrast, rheopexy involves an increase in the fluid's viscosity with time under constant shearing. Both thixotropy and rheopexy are possible to be in combination with any of the previously mentioned flow behaviours exhibited by non-Newtonian fluids.

According to [13, 21], the lubricants rheological properties are commonly assessed through viscosity measurement, a method recognized for its speed, accuracy, and reproducibility.

3. MATERIAL AND METHODS

The current investigation focuses on the examination of lubricating fluids derived from mineral oil, incorporating a viscosity index additive. The choice of particular oil and its corresponding additive is guided by a survey and comparative analysis of the properties and behavior inherent in lubricants designed for journal bearings, a subject extensively explored in the experimental study [4].

The experiment employs the general-purpose industrial oil AN46 (Prista Oil, Bulgaria), with a viscosity grade of ISO VG 46 (according to the viscosity classification ISO 3448-75). Introducing the viscosity index improver, Polybutene 30 (PIB30) (Kemat, Belgium), in various concentrations is a key aspect of our methodology. The study covered a range of seven different additive concentrations, spanning from 0%, 0.3% to 5%. In the text below, the percentage ratios for the concentrations presented are expressed in weight percentages (w. %).

All samples (oil with additive) are measured with an accuracy of 1.10^{-3} g on a calibrated electronic balance Ainsworth DE-310. The solutions are homogenized for five hours at a temperature of ~50°C with continuous stirring with a MSH 300/BOECO magnetic stirrer. The oil samples with seven different concentrations of the additive are prepared in one cycle within a short time and under the same ambient conditions, and in quantities sufficient to carry out all the experiments (200 ml for each concentration).

As previously stated, the incorporation of the modifying additive into the oil imparts non-Newtonian properties to the fluid. By reason of this, experiments are conducted using the suitable Brookfield rotational viscometer of series "CAP 2000+" [22, 23], specifically designed for such kind of lubricants.

The rotational viscometer utilized in the research is of the cone-plate type, as the schematic view of its components is depicted in Fig. 1.a, while a scheme of cone-plate type contact is shown in Fig. 1.b. Within this apparatus, the cone angle θ is instrumental in delivering a consistent shear rate to the fluid, which is situated between the two device components - the rotary cone (spindle), constituting the moving element, and the stationary plate. The range of the measured viscosity is contingent upon factors such as angular velocity ω, as well as the specific shape and dimensions of the employed cone (cone radius - r).

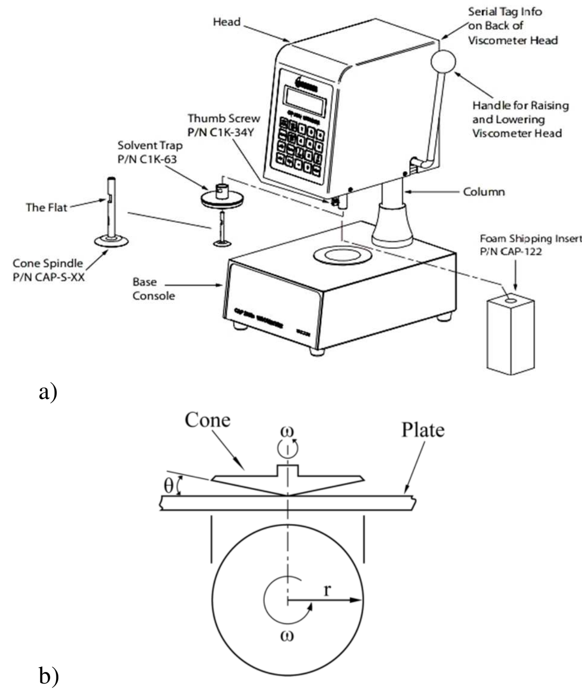

Fig. 1. Rotational viscometer Brookfield "CAP 2000+": a) Components, [22]; b) Cone plate type contact, [16]

In the current experimental investigation, two distinct rotating cones of the viscometer are employed respectively CAP-08 and CAP-03; each characterized by respective geometries and shear rate ranges (CAP-08: $\theta = 3^o$, $r = 15.11$ mm; CAP-03: $\theta = 0.45^o$, $r = 9.53$ mm). The specified shear rate values are categorized, as follows: a range from 200 to 2 000 s^{-1} (for CAP-08), referred to as the "small range" in the text below, and another range spanning from 1 333 to 13 333 s^{-1}(for CAP-03), denoted as the "large range" in the text.

4. RESULTS AND DISCUSSIONS

The results obtained refer to an examination conducted on various oil samples utilizing the above-mentioned Brookfield rotational viscometer.

The presented experimental results demonstrate the correlations between shear stress and shear rate, as well as viscosity and shear rate. It is investigated how the flow behavior is affected by the range and change of shear rate, as well as by the concentration of additives in lubricating oil.

Figure 2 provides rheograms that represent the relationship between shear stress and shear rate at the large range of shear rates, spanning from 1 333 to 13 333 s^{-1}.

These rheograms specifically refer to three lubricant samples distinguished by varying concentrations of the additive (AN46 + resp. 0.3%, 1%, and 4% PIB30). The outcomes reveal the trend that there is a rise in shear stress values with the shear rate increasing (but not linearly as in a Newtonian fluid).

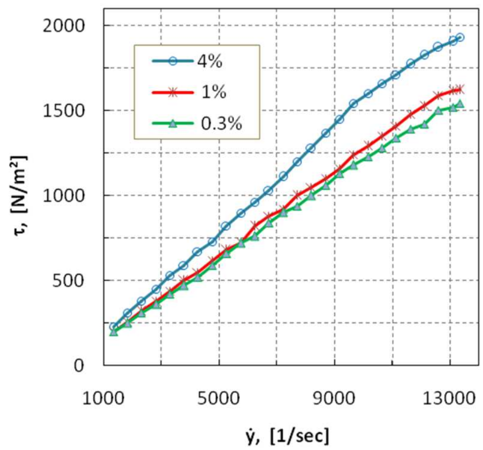

Fig. 2. Shear stress vs. shear rate, additive concentrations 0.3; 1; 4 % (large range of $\dot{\gamma}$)

Analogous rheograms for the case of a small shear rate range (from 200 to 2000 s^{-1}) are shown in Fig. 3, where the results for three other lubricant samples (AN46 + resp. 1%, 3%, 5% PIB30) are presented. Here, the same trend of the relationship between shear stress and shear rate is observed.

Furthermore, the results in Fig. 2 and Fig. 3 show that the values of shear stress increase with increasing the additive concentration. This effect is most visible at large values of τ. The relationship shear stress – shear rate is not a straight line, which should mean that the lubricant under study (mineral base oil blended with polyisobutylene) has a non-Newtonian behaviour. The same tendency for the shear stress of the investigated lubricant (obtained after adding polyisobutylene, which is used in practice as a VI improver, to spindle oil) was also observed in [4].

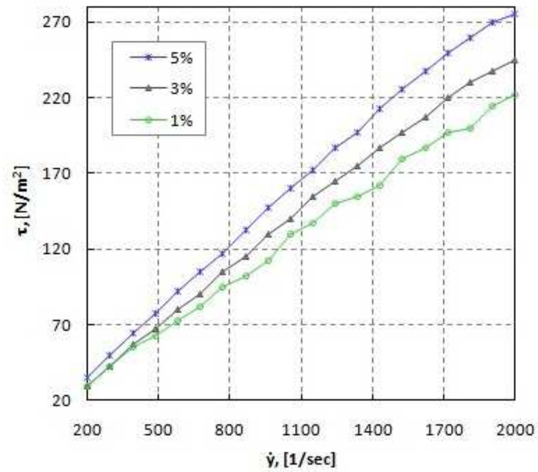

Fig. 3. Shear stress vs. shear rate, additive concentrations 1; 3; 5 % (small range of $\dot{\gamma}$)

The viscosity-shear rate flow curves in Fig. 4 and Fig. 5 refer to samples with additive concentrations of 0%, 3%, 5% in the large shear rate range, and concentrations of 0%, 2%, 5% in the small range, respectively. Notably, the results indicate an increase in viscosity with increasing concentration of the additive. Moreover, there is a decrease in viscosity with increasing shear rate, which is consistent with the characteristic behavior of pseudoplastic fluids [17, 19].

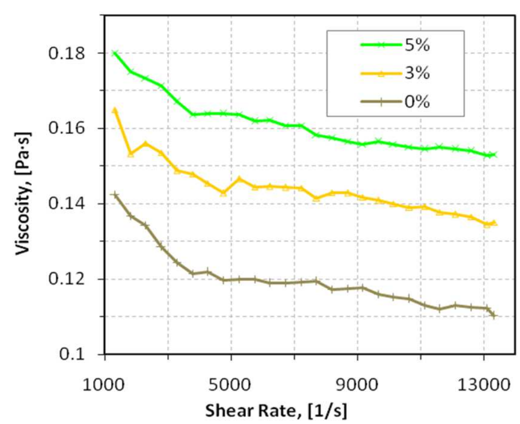

Fig. 4. Viscosity vs. shear rate - additive concentrations 0; 3; 5 % (large range of $\dot{\gamma}$)

It should be noted that all the graphs presented in the last-mentioned four figures show agreement with the theoretical formulations related to this type of non-Newtonian fluids, [4, 17-21].

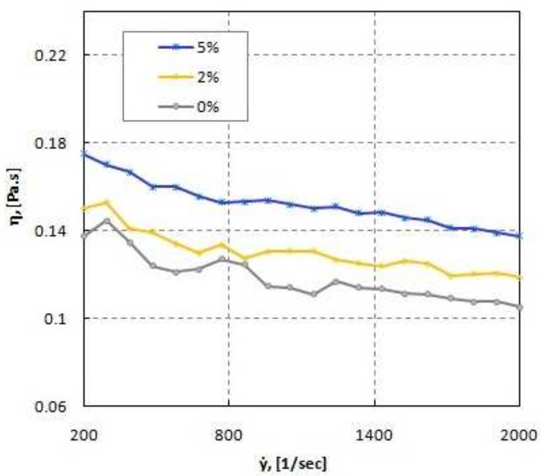

Fig. 5. Viscosity vs. shear rate - additive concentrations 0; 2; 5 % (small range of $\dot{\gamma}$)

The effect of additive (viscosity index improver) concentration on the viscosity η is also illustrated in Fig. 6.

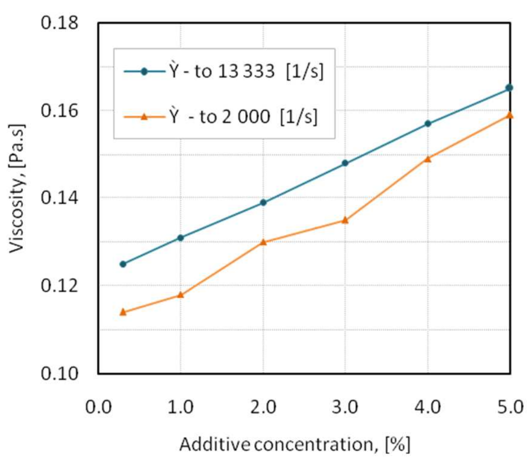

Fig. 6. Relationship viscosity - additive concentration

Obviously, an increase in viscosity is affected by an increase in the concentration of the additive. The viscosity corresponding to each concentration shows higher values within the large shear rate range, in contrast to those observed in the small range. A similar trend regarding the impact of VI improver concentration on lubricant viscosity is established through experimental observations in the study on pseudoplastic fluids [4]. Analogical observations on the effect of VI modifier concentrations on the viscosity of lubricants were also reported in [14, 24-26].

The more precise rheological characterization of the considered lubricant samples (lubricating mineral oil with polymeric additive) suggests the study of these non-Newtonian fluids under dynamic conditions, i.e. when subjected to different shear rates during the time, for example.

The results in Fig. 7 and Fig. 8 (different additive concentrations; large range of $\dot{\gamma}$) illustrate the relationships $\tau - \dot{\gamma}$, $\eta - \dot{\gamma}$ for a longer time of shearing, with the fluid is loaded to a certain value (maximum shear rate), then immediately unloaded to the starting point (minimum shear rate) [16, 21].

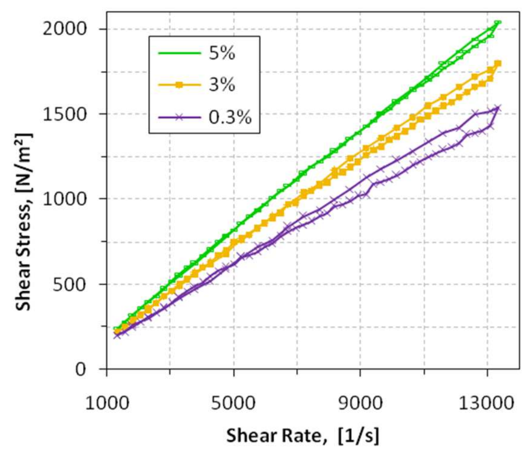

Fig. 7. Shear stress vs. shear rate, additive concentrations 0.3; 3; 5 % (large range of $\dot{\gamma}$)

It is evident that the so called "up" and "down" curves in figures do not overlap and form loops. The same effects are noted also in other experimental studies, for example [27]. The observed hysteresis loops in the flow and viscosity curves are caused by the decrease in fluid viscosity with increasing shear time. Furthermore, the results presented show that the loop area decreases with increasing additive concentration in the lubricant. Therefore, as the concentration of the additive increases, the area of the hysteresis curve decreases and the oils become more stable. Shear stability during operation is an important indicator for oils used in tribo assemblies under conditions of high speeds and/or high loads [8].

In this regard, to the advantages of VI improvers should also be added friction reduction, pour point depression, and dispersion, for which reason they are also known as multi-functional viscosity modifiers [28].

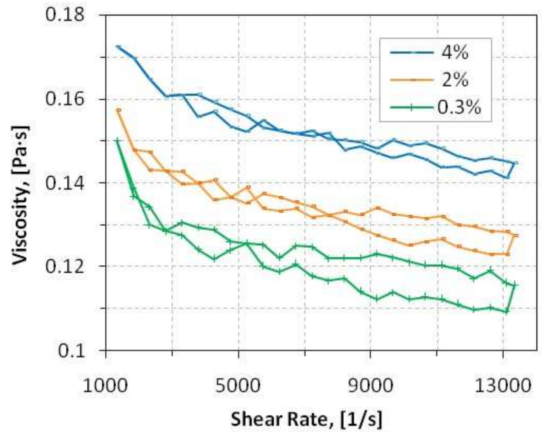

Fig. 8. Viscosity variation with shear rate, additive concentrations 0.3; 2; 4 % (large range of $\dot{\gamma}$)

Fig. 9 shows the effect of "up-down shear rate" on shear stress (at large and small range of $\dot{\gamma}$), while Fig. 10 and Fig. 11 represents the same effect on viscosity (also at both speed ranges of shear rate). The results in these three figures refer to samples with different concentration of the additive.

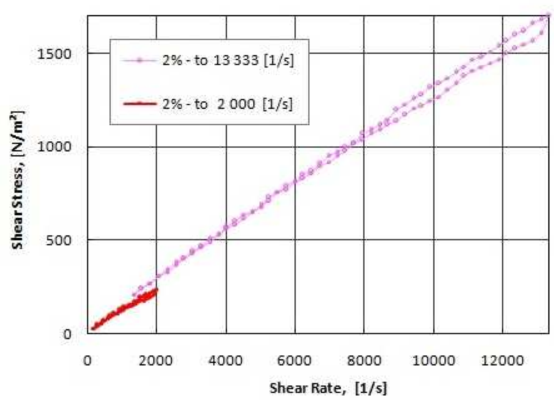

Fig. 9. Effect of shear rate on shear stress for additive concentration 2 % -small and large ranges of $\dot{\gamma}$

The experimental procedure employs the "Up-Down Rate Ramp" test, wherein the fluid is subjected to loading to the maximum shear rate followed by unloading to the initial rate [16, 21]. In this instance, the presence of non-matching curves (for τ and η) indicative of a hysteresis loop is found, which is due to the extended duration of shearing during the experiment.

The decrease in viscosity with an increase in shear rate, indicative of pseudoplastic fluid behavioUr, is explained by a temporary alteration in the structure of molecules of the sample.

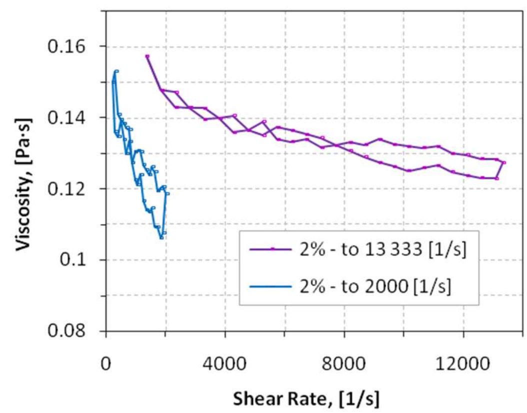

Fig. 10. Effect of shear rate on the viscosity, 2% additive concentration - hysteresis loop, both ranges of $\dot{\gamma}$

The macromolecular structures align almost parallel to the spindle surface, facilitating its rotation and leading to a reduction in viscosity [16].

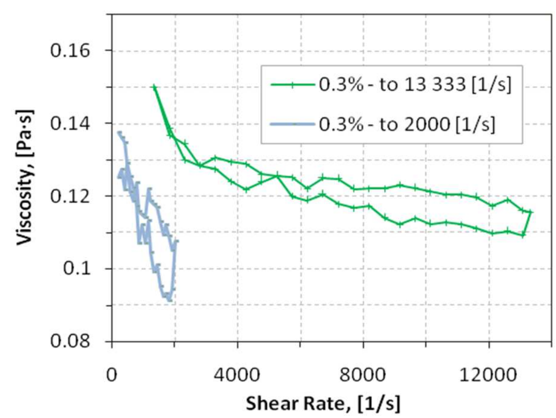

Fig. 11. Hysteresis loop for viscosity curves, 0.3% additive concentration, (both ranges of $\dot{\gamma}$)

When the shear rate decreases, there is a corresponding reversal in the process, resulting in a rising of viscosity. The absence of a match between the two curves during the sequence of growing and subsequently diminishing shear rates (manifested by the presence of a hysteresis loop) is attributed to the influence of the time factor. In our specific case, the tested fluid exhibits characteristic thixotropic properties during this process.

In this sense, it is confirmed here that most materials exhibiting shear thinning (pseudoplastic) behaviour are usually thixotropic, as it takes a time for the necessary rearrangements in microstructural elements to cause the shear thinning effect [18].

5. CONCLUSIONS

This study presents the findings of an experimental investigation into the impact of the viscosity-index additive Polybuten PIB30 on mineral oil AN46 and its consequential influence on the rheological behavior of the resulting lubricating fluid, characterized by non-Newtonian properties.

Graphical representations of the experimental findings highlight the interrelationships between shear stress and shear rate, as well as between viscosity and shear rate. Additionally, the study explores the effects of varying shear rates and the influence of additive concentration.

The experimental samples, featuring different concentrations of the polymeric thickening additive, exhibit typical pseudoplastic fluid behavior. As the shear rate increases, there is a corresponding decrease in viscosity and an increase in shear stress. The influence of increasing additive concentration is evident in the rise of shear stress and an increase in viscosity.

Furthermore, the lubricants tested display characteristic thixotropic properties. This implies that their viscosity decreases over time when subjected to constant shearing at a consistent rate. Overall, these comprehensive findings contribute to a deeper understanding of the rheological characteristics of the lubricating fluids under investigation, providing valuable insights into their behavior under varying conditions.

Acknowledgments

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Rheologische Charakterisierung von Mineralölen mit Additiven

Abstrakt: Viskositätsindexverbesserer mildern die Empfindlichkeit der Schmierstoffviskosität gegenüber Temperaturänderungen. Diese Studie untersucht den Einfluss verschiedener Konzentrationen des Additivs dieses Typs Polybuten 30 (PIB30) auf das Mineralgrundöl AN46, indem ein Kegel-Platte-Rotationsviskosimeter verwendet wird, um rheologische Eigenschaften bei mittleren bis hohen Schergeschwindigkeiten zu bewerten. Die Ergebnisse deuten auf typische nicht-Newtonsche Eigenschaften der Proben hin, d. h. pseudoplastisches Flüssigkeitsverhalten, wobei eine zunehmende Scherrate zu einer erhöhten Scherspannung und einer verringerten Viskosität führt. Konzentrationsabhängige Trends zeigen einen Zusammenhang zwischen Additivkonzentration, erhöhter Viskosität und Scherspannung. Die untersuchten Schmierstoffe zeigen typische thixotrope Eigenschaften.

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