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Tribological properties of trimethylolpropane trioleat as hydraulic fluids blended with anti-wear additives

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KEYWORDS

Trimethylolpropane
Trioleat
Hydraulic Fluids
Wear Scar Diameter
Coefficient of Friction

ABSTRACT

Environmental concerns about hydraulic fluids have spurred research into biobased alternatives to conventional mineral oils. Among these alternatives, TMP trioleate, derived from triglycerides, stands out due to its high biodegradability and potential as a sustainable hydraulic fluid. However, achieving adequate wear resistance remains a challenge in high-performance applications. In this study, the tribological properties of TMP trioleate were investigated by incorporating zinc dialkyl dithiophosphate (ZDDP), di-n-butyl phosphite (DnBP), low-zinc industrial hydraulic fluids additives (HFA1), and ashless industrial hydraulic fluid additive (HFA2) to enhance its lubricating capabilities and wear resistance. A Fourball Tester was used based on ASTM 4172-21 to measure wear scar diameter (WSD) and coefficient of friction (COF), while microscopy image analysis provided insights into the wear scar diameter image. HFA2 demonstrated the best performance, achieving the lowest WSD (323.23 μm) and COF (0.04496) at 0.9% concentration. ZDDP performed well at 3% concentration with a WSD of 351.18 μm, while DnBP showed good wear reduction at 1.2% (325.25 μm). In contrast, HFA1 was less effective, showing the largest WSD (513.16 μm) at 1.2%. Trimethylolpropane trioleat (TMPTO) demonstrated moderate friction reduction (COF 0.07509) but required additives to improve wear resistance. These findings support TMPTO, particularly with optimized additive blends, as an eco-friendly alternative to mineral-based hydraulic fluids.

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1.0 INTRODUCTION

Hydraulic fluids play a crucial role in industrial and mechanical systems, where they facilitate power transmission, lubrication and cooling within hydraulic machinery (Quilumba et al., 2014). The performance and longevity of these systems significantly depend on the hydraulic fluid's tribological properties - such as friction reduction, wear resistance, and load-carrying capacity - which are critical in minimizing component degradation under high pressure and continuous operation (Li et al., 2024). In recent years, the demand for sustainable and high-performance hydraulic fluids has surged, leading to increased interest in bio-based fluids as potential alternatives to conventional mineral oils (Li et al., 2024).

The four-ball test is a vital method for evaluating the performance of lubricants, particularly in assessing their effectiveness under boundary lubrication conditions, where metal-to-metal contact is most likely to occur. This test measures two critical parameters: Wear scar diameter (WSD) and coefficient of friction (COF). A smaller WSD indicates a lubricant's ability to minimize material loss and surface damage, while a lower COF reflects its effectiveness in reducing friction. In boundary lubrication, the protective layer formed by the lubricant is crucial for preventing direct contact between surfaces, thereby enhancing operational efficiency and longevity under extreme pressure and minimal film thickness.

The relevance of the four-ball test extends to hydraulic fluids and bio-lubricants, as both categories benefit from the insights gained through this evaluation method. Hydraulic fluids, essential for power transmission in various industrial applications, require additives that can improve their anti-wear and extreme-pressure properties, which can be assessed using the four-ball test (Bachchhav et al., 2023). Similarly, bio-lubricants, derived from renewable sources, have shown promising tribological performance, often matching or exceeding that of conventional lubricants (Cecilia et al., 2020; Ojaomo et al., 2024). Research indicates that bio-lubricants can provide excellent lubricity, low volatility, and high viscosity index, making them suitable for applications where traditional mineral oils have been used (Cecilia et al., 2020; Ojaomo et al., 2024). The integration of bio-lubricants into hydraulic systems not only enhances environmental sustainability but also aligns with the growing demand for eco-friendly solutions in engineering practices, demonstrating that both hydraulic fluids and bio-lubricants can benefit from rigorous testing such as the four-ball test to ensure optimal performance and minimal environmental impact.

Trimethylolpropane trioleate, a bio-based ester, has garnered attention as a promising candidate for hydraulic applications due to its excellent lubricating properties, biodegradability, and compatibility with a range of additives. This ester is synthesized from palm oil using trimethylolpropane (TMP) as the reactant through an esterification process (Samidin et al., 2021; Wu et al., 2015), TMP trioleat offers a viscosity range 20-100 mm2/s, with an optimal viscosity of approximately 46 mm^2/s at 40°C, a standard for ISO 46 oils (Chang et al., 2015). TMP trioleate's molecular structure provides high oxidative stability and low-temperature fluidity (Z. Yang et al., 2023), which are desirable traits for hydraulic fluid applications. However, despite its inherent advantages, the performance of TMP trioleate in high-stress, wear-intensive applications necessitates further improvement. To further minimize wear and friction in the system, small amounts of weight percentage of additives are added to the lubricant base stock to improve and enhance the oil properties. Those additives can be anti-wear (AW), extreme pressure (EP), anti-corrosion, and anti-foam (Jason et al., 2020).

This study investigates the tribological behavior of TMP trioleate when blended with specific anti-wear additives, aiming to assess the fluid's performance in reducing friction and wear. By evaluating the effects of these additives on TMP trioleate's tribological properties, this research seeks to advance the development of bio-based hydraulic fluids that meet or exceed the standards of traditional mineral oil-based fluids, thereby contributing to a more sustainable approach in hydraulic systems.

2.0 EXPERIMENT AND METHODS

The methodological framework adopted in this study is summarised in Figure 1, which delineates the workflow into two principal phases. In Phase 1, the tribological properties of trimethylolpropane trioleate (TMPTO) were systematically evaluated to assess its suitability as a biobased hydraulic fluid with enhanced wear resistance. Additives such as zinc butyl octyl primary alkyl dithiophosphate (ZDDP), di-n-butyl phosphite (DnBP), low-zinc industrial hydraulic fluids additive (HFA1), and ashless industrial hydraulic fluids (HFA2) additives were incorporated. The preparation of lubricant samples involved precise mixing of the base oil TMPTO with specific additives using an ultrasonic homogenizer. This ensured a uniform and stable dispersion of the additives in the base oil, critical for consistent tribological performance during testing.

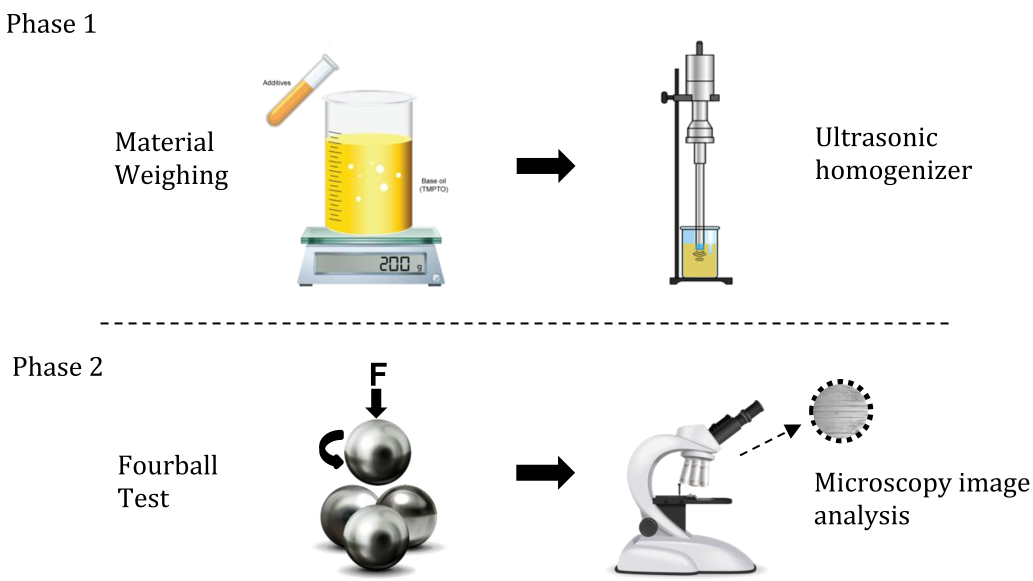


Figure 1: Methodology adopted for the present study.

Phase 2 comprised the evaluation of tribological performance using a Fourball Tester, enabling a comparative analysis of both anti-wear and frictional behaviour across the formulated samples. Two key performance indicators were assessed WSD and COF. The WSD was measured using optical microscopy to quantify surface damage on the steel balls, providing insights into the anti-wear capabilities of each formulation. COF data, recorded in real-time during testing, offered an additional perspective on the lubricating efficiency and frictional stability of the samples under boundary lubrication regimes. In this study, the microscopy analysis was limited to WSD measurement, without further examination of surface morphology or wear mechanisms.

2.1 Materials and Sample Preparation

Trimethylolpropane Trioleate (TMPTO), Bio VG, and mineral hydraulic oil (MO) were used as base fluids in this study. The physical properties of these samples are summarised in Table 1. Zinc butyl octyl primary alkyl di-thiophosphate (ZDDP), Di-n-butyl phosphite (DnBP), a low-zinc industrial hydraulic fluid additive (HFA1), and an ashless industrial hydraulic fluid additive (HFA2) were selected as additives, with their physical properties provided in Tables 2 and 3. Acetone (>99.5% purity) was used as a cleaning solvent. All materials and chemicals were used as received without further purification.

Table 1: Physicochemical properties of samples.

Properties	TMPTO[1]	Bio VG[2]	MO[3]
Density at 15°C (g/cm^3)	0.916	0.9126	0.856
Kinematic Viscosity at 40°C (cSt)	45	46	46
Kinematic Viscosity at 100°C (cSt)	9.5	8.3	6.9
Viscosity Index	202	182	105
Pour Point (°C)	-40	0	-30
Flash Point (°C)	300	218	230

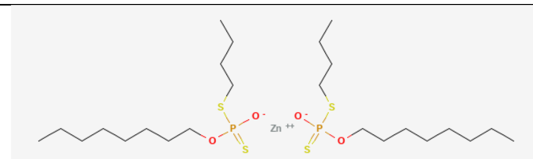
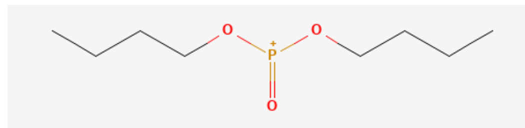
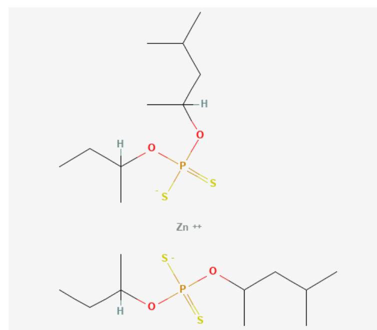
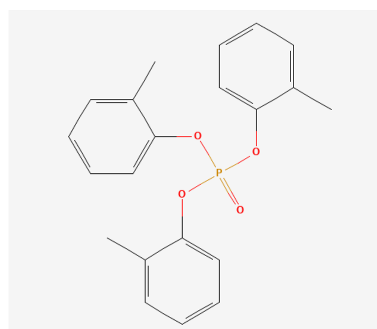
[1] Trimethylolpropane trioleat, Radialube 7364, Oleon NV
[2] Bio VG 46, UWM Grantt International Sdn. Bhd
[3] Shell Tellus S2 MX 46, Shell

Table 2: Hydraulic additives physical properties (Chorus, 2024).

Properties	ZDDP	DnBP
Density at 20°C (g/cm^3)	1.108	
Kinematic Viscosity at 100°C (mm/s)	11.34	
Flash Point	195	
Zinc (% wt.)	8.81	
Sulfur (% wt.)	15.99	14.5-16
Phosporus (% wt.)	7.8	-
Properties	**HFA[1]**	**HFA[2]**
Density at 20°C (g/cm^3)	1.038	
Kinematic Viscosity at 40°C (mm/s)	19.35	
Flash Point	112	>110
Zinc (% wt.)	-	3.65
Sulfur (% wt.)	7.61	7.8
Phosporus (% wt.)	3.56	3.18

In this study, an ultrasonic homogenizer apparatus, specifically the LABSONIC® P, was used to blend additives with TMPTO base oil, ensuring a uniform dispersion of additive molecules throughout the mixture. The LABSONIC® P operates at cycle 0.5 and amplitude 60%, generating rapid micro-cavitations in the fluid that break down and disperse additive particles effectively. This process enhances the compatibility and stability of the additives within the fluid matrix.

Table 3: A summary of additives.

Additive	**Chemical Formula**
ZDDP[a]	
Di-n-butyl Phosphite[b]	
Low Zinc additives, HFA1[c]	
Ashless additives, HFA2[d]	

a. National Center for Biotechnology Information (2024). PubChem Compound Summary for CID 57360050, ZINC butyl octyl dithiophosphate. Retrieved December 16, 2024 from https://pubchem.ncbi.nlm.nih.gov/compound/ZINC-butyl-octyl-dithiophosphate.

b. National Center for Biotechnology Information (2024). PubChem Compound Summary for CID 6327349, Dibutyl phosphite. Retrieved December 16, 2024 from https://pubchem.ncbi.nlm.nih.gov/compound/Dibutyl-phosphite.

c. National Center for Biotechnology Information (2025). PubChem Compound Summary for CID 22833364, Phosphorodithioic acid, mixed O,O-bis(sec-Bu and 1,3-dimethylbutyl) esters, zinc salts. Retrieved April 21, 2025 from https://pubchem.ncbi.nlm.nih.gov/compound/22833364.

d. National Center for Biotechnology Information (2025). PubChem Compound Summary for CID 22833364, Phosphorodithioic acid, mixed O,O-bis(sec-Bu and 1,3-dimethylbutyl) esters, zinc salts. Retrieved April 21, 2025 from https://pubchem.ncbi.nlm.nih.gov/compound/22833364.

The blending process was conducted for approximately 30 minutes, which was determined as an optimal time frame to achieve a homogeneous mixture without compromising the chemical integrity of the additives. During the process, the amplitude was set 60% of the maximum output, allowing for fine control over the cavitation intensity. The volume capacity of samples is 200 g, which was suitable for the scale of this study. Additionally, the homogenizer was set to operate in intervals of 10 minutes to monitor and control any temperature rise in the sample, ensuring the stability of the additives during the blending process. This setup facilitated the production of a stable and uniform formulation, ready for further tribological testing. The stability of the blend was preliminarily confirmed through visual observation, with no signs of phase separation or sedimentation detected during a 14-day storage period at ambient conditions.

2.2 Tribological Test

The tribological experiments were conducted using a commercial tribometer (DUCOM) with a fourball test configuration (Ducom, 2009). This setup, adhering to ASTM D4172 standards, creates a controlled point-contact scenario between the test balls, closely simulating real-world lubrication conditions. In this configuration, three chromium steel balls (G20 grade, ISO 3290 compliant) are securely arranged in the oil chamber and fully immersed in the lubricant is shown in Figure 2, with a fourth ball pressing from above to form the sliding contact, before starting a series of tests, four new balls for each test run were cleaned using acetone and dried with dry air. The applied load was 40 N, and the rotational speed was maintained at 1200 rpm (0.456 m/s) to simulate operational stresses. A thermocouple monitored lubricant temperature directly within the oil chamber, and a built-in heater with an automatic controller stabilized the test temperature at 75 °C. After each 60 min friction test, three balls at the bottom base were washed with acetone. This configuration enabled precise, real-time measurements of frictional behavior and wear characteristics under defined load and speed parameters, providing robust data for evaluating lubricating performance.

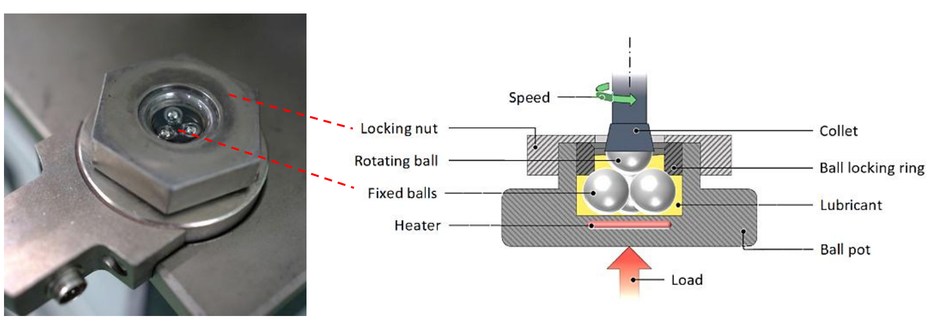


Figure 2: Schematic of tribological test use four-ball tribotester (Ducom, 2016)

2.3 Characterization of Test

The coefficient of friction (COF) was calculated using a formula as described in ASTM D5183, the formula uses torque and normal load values of the test and a normalization factor to calculate friction coefficient. The absolute torque and load values were received during tests from the Ducom assisting the four ball tribometer.

The COF is a crucial parameter in tribological studies, particularly when evaluating lubricant performance using the four-ball test method. For this test, the COF can be calculated using the following formula, as shown in Equation (1):

$$\mu = \frac{T\sqrt{6}}{3Wr} \quad (1)$$

where, μ is coefficient of friction, T is frictional torque (kg/mm), W is applied load in (kg) and r is distance from the center of the contact surfaces on the lower balls to the axis of rotation, which is 3.67mm.

Microscopy images analysis of the wear scars was obtained using a Shodensha GR3400 microscope. These images provided detailed insights into surface morphology, allowing analysis of wear patterns, scar depth, and surface roughness, among other factors. However, in this study, the microscope was specifically utilized to measure the diameter of the wear scars on the balls. By capturing magnified images of the sample's surface, this microscope enables qualitative analysis of roughness levels by visualizing surface irregularities, asperities, and micro-scratches that contribute to the overall texture.

3.0 RESULTS AND DISCUSSION

3.1 Coefficient of Friction Characterization

The synergistic effect of appropriate additive concentrations enhanced the tribological performance of the lubricant. Therefore, it is essential to optimize additive concentration. Based on numerous reports in previous studies (Wen et al., 2024), four different concentrations of different additives were prepared. These definitions are listed in Table 4. The concentration of each anti-wear additive was not unified across all formulations but was instead selected based on the manufacturer's recommended dosage range to ensure optimal functionality within the TMPTO base oil matrix. This approach minimises the risk of additive overdosing or underperformance and reflects practical formulation methods used in industrial lubricant design. Despite the varying %wt, all additives were evaluated under identical tribological test conditions, ensuring a reliable and insightful comparison of their effectiveness in minimizing friction and wear.

Table 4: Different concentrations of the four additives.

Additive	ZDDP			DnBP			HFA[1]			HFA[2]		
wt. %	1	2	3	0.3	0.6	0.9	0.4	0.6	0.8	0.2	0.4	0.6

The selection of varying additive concentrations was selected to represent low, medium, and high levels, with the medium dosage aligning with the manufacturer's recommended value (Chorus, 2024) and serving as a reference point for performance benchmarking. The lower and higher concentrations were derived by proportionally adjusting around this baseline to explore under and over treatment effects without exceeding formulation safety thresholds.

Excessive dosing of ZDDP can lead to tribofilm overgrowth, resulting in rough and unstable zinc phosphate layers that elevate friction and wear under dynamic loading conditions (Spikes, 2025). In contrast, suboptimal levels of DnBP may fail to activate effective boundary lubrication, especially given its ashless phosphite nature (Luiz and Spikes, 2020). HFA1 and HFA2, formulated as low-zinc and ashless packages respectively, exhibit distinct sensitivity to dosage, excessive levels may disrupt base oil interactions, while insufficient dosing may not achieve the desired anti-wear protection (H. Li et al., 2022).

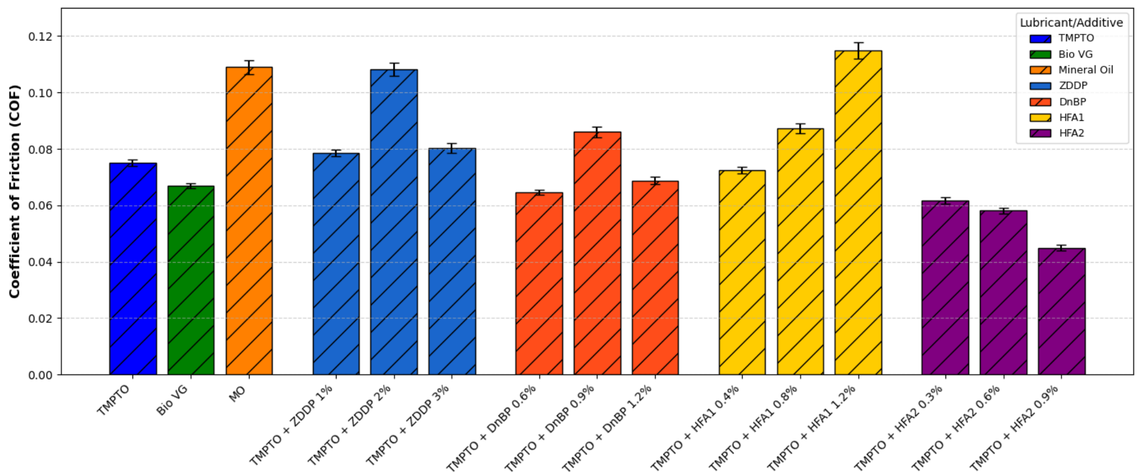


Figure 3: Comparison of coefficient of friction various hydraulic fluids.

The experiment compared the friction levels COF of different lubricants and their additives formulations, as shown in Figure 3. The base lubricant, TMPTO, had a COF of 0.07509, while Bio VG was slightly better with a COF of 0.06691. In contrast, Mineral Oil exhibited a significantly higher COF of 0.10902, indicating less effective friction reduction compared to the biobased lubricants (Rudnick, 2020).

The high content of polar molecules, particularly the polyunsaturated fatty acids TMPTO, contributes to the formation of a stable lubrication film. This characteristic explains the lower average COF observed for TMPTO compared to mineral oil-based hydraulic fluids, as depicted in the graph shown in Figure 4. Notably, the COF of TMPTO closely approaches the performance of Bio VG, even without the addition of anti-wear additives. The superior lubricity provided by TMPTO highlights its effectiveness in reducing friction, maintaining stability, and improving overall tribological performance under operational conditions (Chanes de Souza et al., 2020; Padgurskas et al., 2011; Zulkifli et al., 2016).

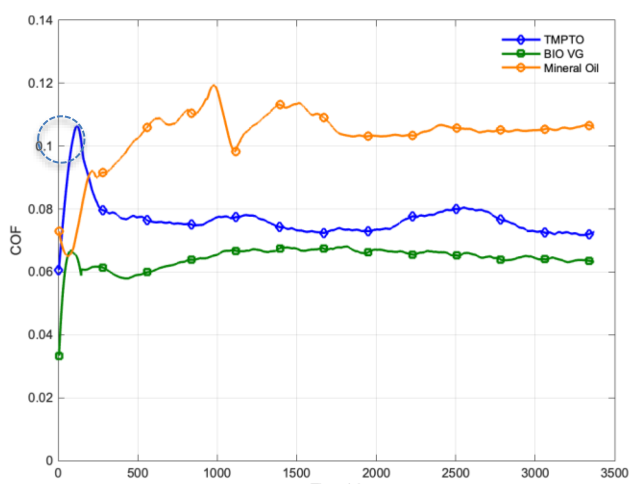


Figure 4: Comparison of COF for TMPTO, bio-VG and mineral oils.

The initial rise in friction, as marked in Figure 4, reflects boundary lubrication conditions where surface contact is predominant due to the absence of anti-wear additives (Bart et al., 2013). As the test progresses, a gradual decrease in COF suggests the onset of mixed lubrication, supported by TMPTO's inherent polarity and surface affinity. Nevertheless, the absence of a pronounced hydrodynamic regime implies limitations in film thickness generation under the applied conditions (Samidin et al., 2021). When compared to Bio VG, which exhibits lower and more stable friction, and Mineral Oil, which shows higher variability and frictional resistance, TMPTO demonstrates intermediate behaviour. These findings suggest that TMPTO offers a functional base oil foundation with moderate tribological performance, which may be further optimized through the application of carefully selected anti-wear additives compatible with its ester structure.

The influence of different anti-wear additives on the COF of TMPTO-based lubricants is illustrated in Figure 5. Each additive exhibits distinct tribological behaviour, depending on its concentration and chemical nature. Adding ZDDP in different amounts (1%, 2%, and 3%) showed varying results, with 2% ZDDP having the highest COF of 0.10818, meaning more friction at this level. As shown in Figure 5a, the average COF for the 2% ZDDP concentration is higher than that of both 1% and 3%. This suggests that at intermediate concentrations, the tribofilm formed is less stable due to partial decomposition and repeated film regeneration under boundary lubrication conditions (Soltanahmadi et al., 2019; Ueda & Spikes, 2024). In contrast, the 1% concentration forms a thinner yet stable boundary film (Dawczyk et al., 2019), while the 3% concentration likely reaches surface saturation, producing a thicker and more uniform tribofilm that results in lower and more consistent friction levels (McDonald, 2017; Spikes, 2025).

Adding Di-n-butyl Phosphite (DnBP) gave good results, especially at 0.6%, with a COF of 0.06459. However, higher amounts of DnBP (0.9% and 1.2%) increased the COF to 0.08599 and 0.06881, respectively. The transient frictional spikes observed at both the initial and final stages of the 0.6% DnBP concentration test suggest delayed boundary film establishment and subsequent film degradation or depletion under prolonged sliding (H. Li et al., 2022). At 0.9% concentration, the elevated coefficient of friction implies the formation of a chemically or mechanically unstable tribofilm, possibly due to excessive phosphite adsorption or non-uniform surface coverage. In contrast, the 1.2% concentration appears to promote the development of a more cohesive and load bearing tribolayer, contributing to a lower and more stable friction regime (Klaus & Bieber, 1964; Sanin et al., 1960).

The low-zinc hydraulic fluid additive (HFA1) demonstrated mixed results. At lower concentrations (0.4% and 0.8%), it maintained moderate friction levels, but at 1.2%, the COF peaked at 0.11485, indicating a significant increase in friction. This suggests that HFA1 is less effective in reducing friction at higher concentrations, likely due to limitations in its tribofilm formation, as similar trends have been identified in previous studies where unstable or insufficient tribofilms resulted in higher COF under boundary conditions (Zhang et al., 2021).

The ashless hydraulic fluid (HFA2) performed the best in reducing friction. Its COF consistently dropped as the concentration increased, reaching the lowest COF of 0.04496 at 0.9%. This suggests that HFA2 could be a good, environmentally friendly alternative to traditional zinc-based additives while still providing excellent performance (Miller et al., 2014). The consistent reduction in COF observed across all tested concentrations of the HFA2 indicates the formation of a stable, low-shear-strength tribofilm. Unlike metallic additives, the organophosphorus-based HFA2 likely promotes uniform film growth without surface interference or abrasive residues (David Phillips and Milne, 2017). The compatibility between HFA2 and the polar ester base oil

(TMPTO) may further enhance boundary film integrity through synergistic adsorption, resulting in superior antiwear performance even at low additive concentrations (He et al., 2024; Kim et al., 2010; Rudnick, 2017).

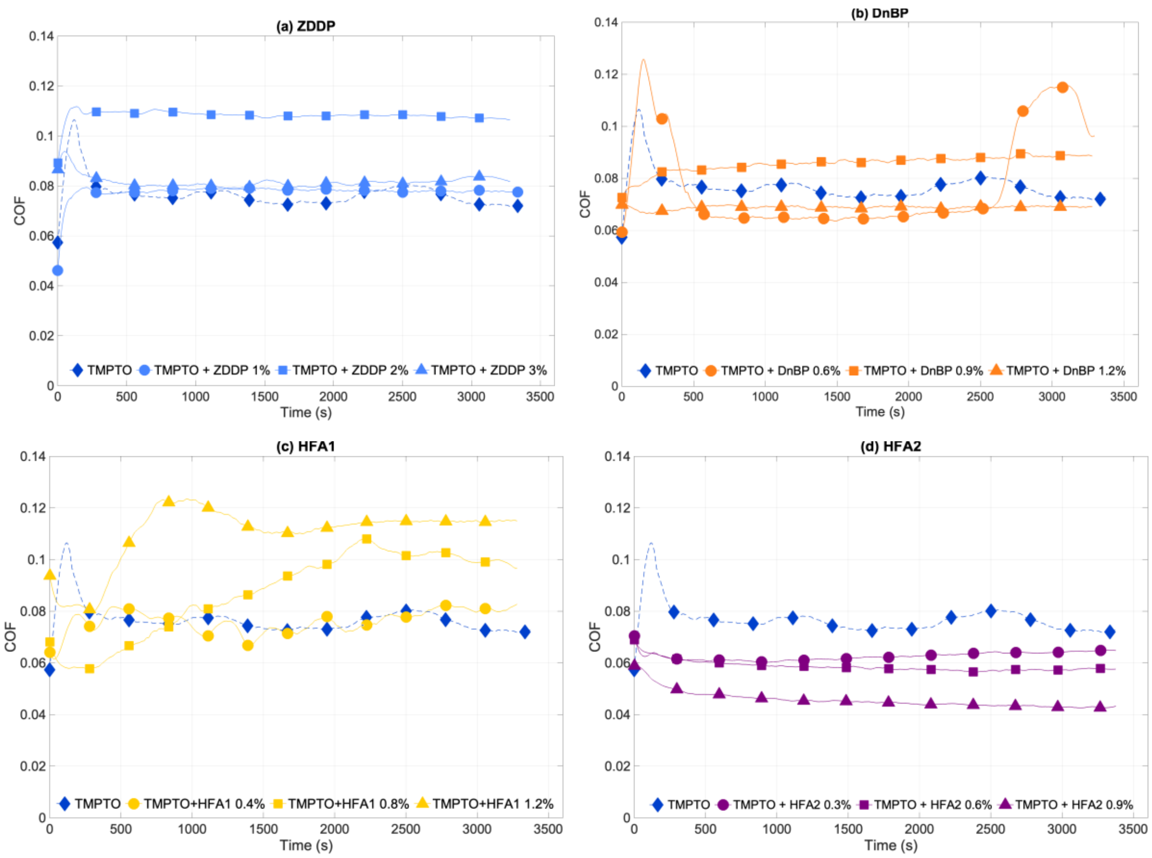


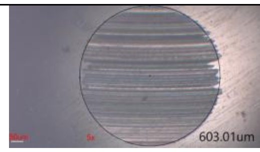
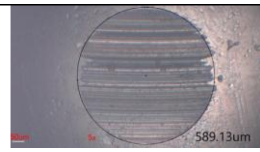
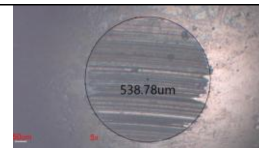
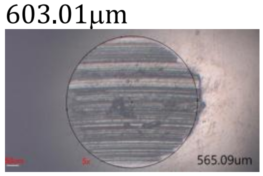
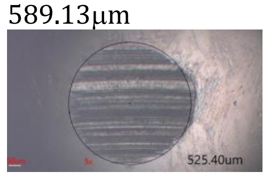
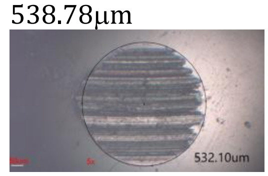
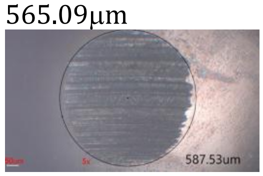
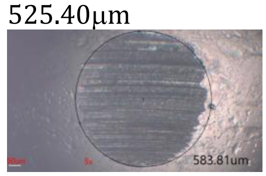
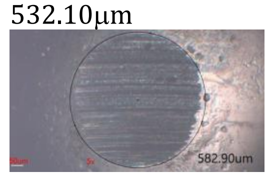
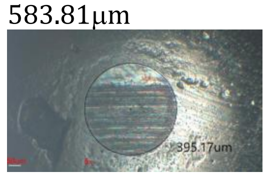
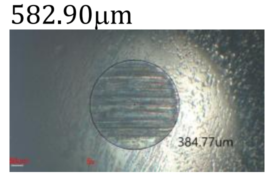
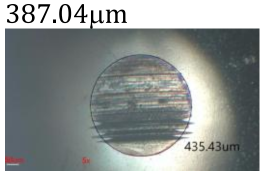
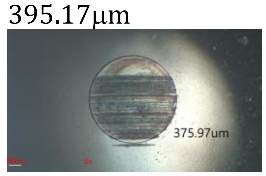
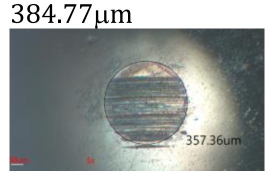
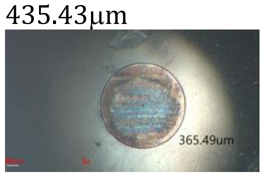
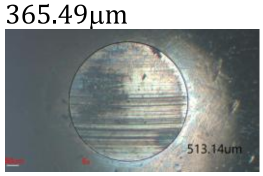
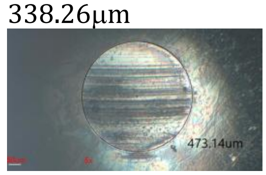
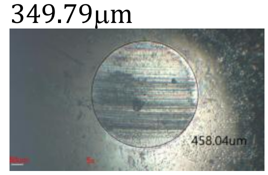
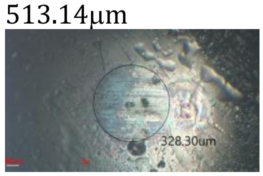
Figure 5: Comparison of COF TMPTO with various antiwear additives

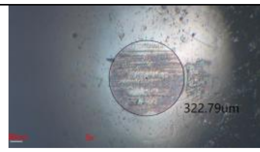
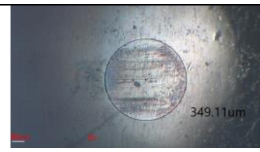
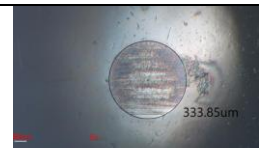
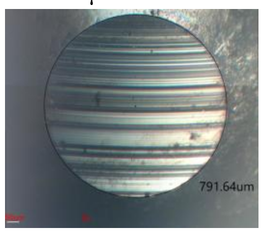
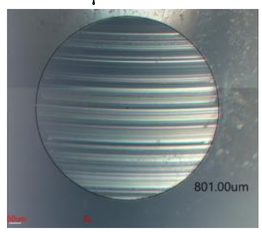
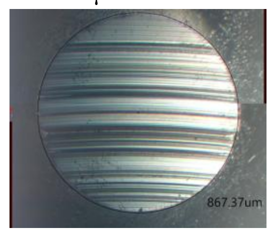
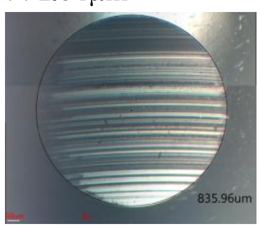
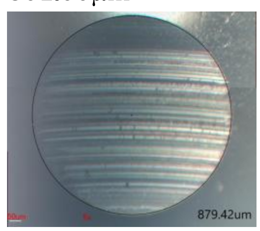
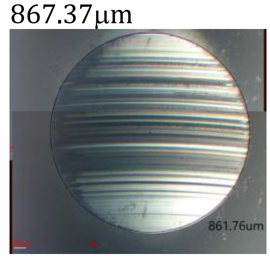
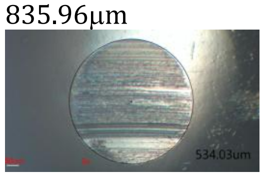
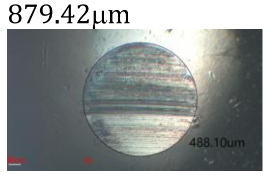
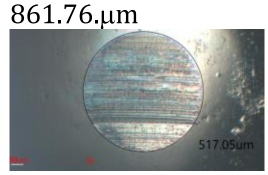
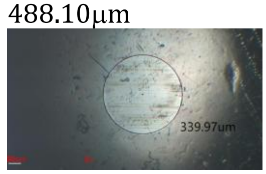
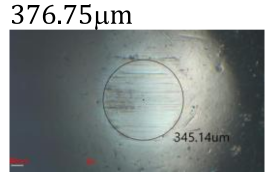
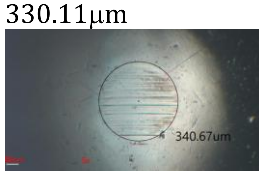
3.2 Wear Characterization

The tribological performance of TMPTO as a base oil for hydraulic fluids, blended with additives, was evaluated alongside commercial Bio VG and mineral oil-based hydraulic fluids using a four-ball tribometer. The results demonstrate that TMPTO exhibits superior anti-wear properties, highlighting its potential as an effective base oil for enhancing the wear resistance of hydraulic fluids.

Table 5 illustrates the variation in Wear Scar Diameter (WSD) of balls lubricated with TMPTO-based lubricants containing different additives. ZDDP exhibits a consistent reduction in WSD with increasing concentration, achieving 351.18 µm at 3 wt. %, highlighting its superior anti-wear performance at higher concentrations. DnBP shows a sharp decrease in WSD at 0.9 wt. %, reaching 329.61 µm, indicating its optimal concentration, with no further improvement at 1.2 wt. %. HFA1 demonstrates minimal effect at lower concentrations but shows a significant reduction to 513.06 µm at 1.2 wt. %, emphasizing the need for higher concentrations. HFA2 provides the most consistent performance, reducing WSD to 323.23 µm at 0.9 wt. %, demonstrating its high efficiency even at low concentrations.

Table 5: Ball wear morphology under 40 N axial force and 75 °C temperature at constant sliding speed (1,200rpm) during 1 h.

	Ball 1	**Ball 2**	**Ball 3**
TMPTO	 603.01μm	 589.13μm	 538.78μm
BIO VG	 565.09μm	 525.40μm	 532.10μm
MO	 587.53μm	 583.81μm	 582.90μm
TMPTO+ZDDP 1%	 387.04μm	 395.17μm	 384.77μm
TMPTO+ZDDP 2%	 435.43μm	 375.97μm	 357.36μm
TMPTO+ZDDP 3%	 365.49μm	 338.26μm	 349.79μm
TMPTO+DnBP 0.6%	 513.14μm	 473.14μm	 458.04μm
TMPTO+DnBP 0.9%	 328.30μm	 341.72μm	 318.81μm

	Ball 1	**Ball 2**	**Ball 3**
TMPTO+DnBP 1.2%	 322.79μm	 349.11μm	 333.85μm
TMPTO+HFA1 0.4%	 791.64μm	 801.00μm	 867.37μm
TMPTO+HFA1 0.8%	 835.96μm	 879.42μm	 861.76.μm
TMPTO+HFA1 1.2%	 534.03μm	 488.10μm	 517.05μm
TMPTO+HFA2 0.3%	 375.82μm	 339.97μm	 376.75μm
TMPTO+HFA2 0.6%	 330.11μm	 332.52μm	 345.14μm
TMPTO+HFA2 0.9%	 340.67μm	 315.86μm	 313.17μm

The influence of varying additive concentrations on the WSD for different TMPTO formulations is presented in Figure 6. It should be noted that the values shown represent the average WSD obtained from the experimental measurements. Furthermore, the selected concentrations were not intended to facilitate direct comparison across additives based on identical weight percentages. Instead, they were determined according to the manufacturers' recommended dosage ranges to ensure that each additive was evaluated under conditions that reflect its optimal performance.

The data clearly indicate that the WSD decreases progressively as the additive concentration increases, demonstrating the effectiveness of the additives in enhancing the anti-wear performance of TMPTO-based hydraulic fluids (Kathamore et al., 2020).

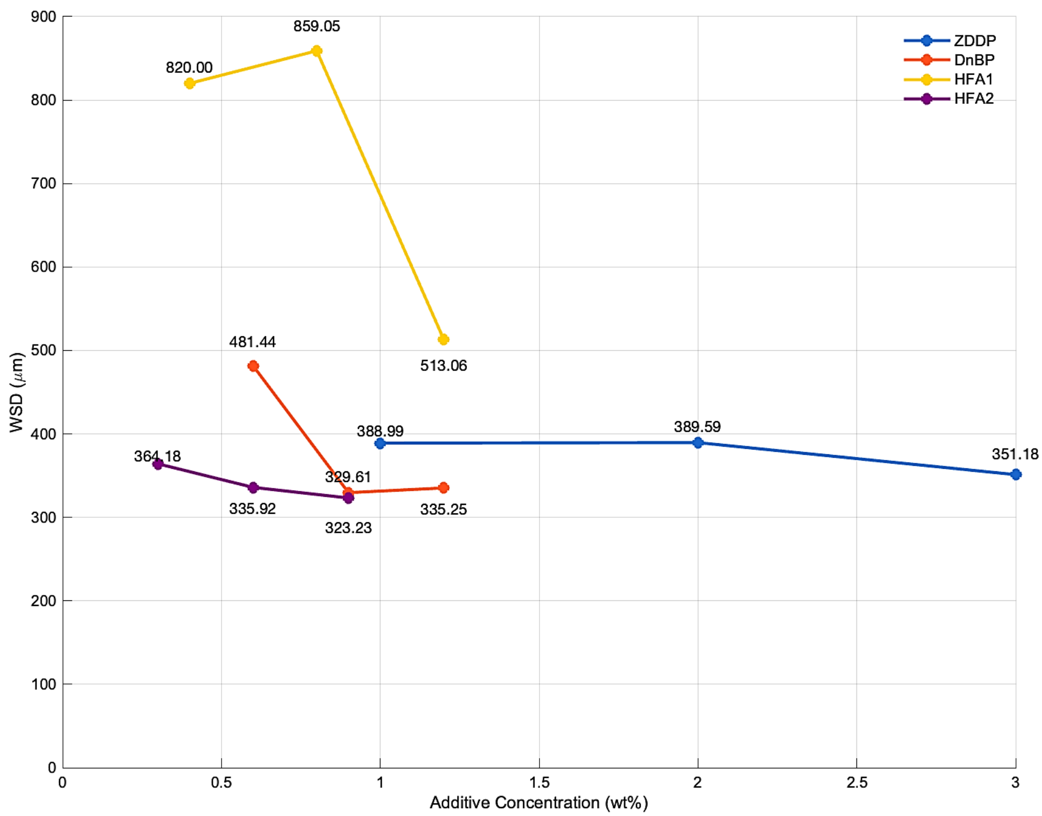


Figure 6: Wear scar diameter for various additives.

3.3 Effect of Antiwear Additives on Hydraulic Fluids

The evaluation of WSD provides insight into the anti-wear performance of lubricants under identical test conditions. Bio VG exhibited the smallest WSD of 540.86 µm, indicating superior anti-wear properties due to its optimized formulation with effective additives. In contrast, TMP Trioleate, tested as a raw base fluid without additives, recorded a higher WSD of 576.97 µm, reflecting moderate wear protection but limited performance in boundary lubrication. Mineral Oil (MO) showed the largest WSD at 584.75 µm, indicating the least effective anti-wear characteristics. These results demonstrate the importance of additive formulations in enhancing the anti-wear properties of base fluids like TMP Trioleate.

3.3.1 ZDDP

At present, most of the sulfur–phosphorus type AW additives are dialkyl dithiophosphate salt. Among them, zinc dialkyl dithiophosphate (ZDDP) is the most common, and its chemical structure is shown in Table 3a (Li et al., 2022). Table 5 shows the effect of ZDDP concentration on the wear scar diameter (WSD) for TMPTO. At lower concentrations (1–2 wt. %), the WSD remains steady at around 390 μm, indicating limited anti-wear improvement. However, at 3 wt. %, a significant reduction in WSD to approximately 351 μm occurs, demonstrating the enhanced anti-wear performance due to the formation of a protective tribofilm.

The tribological mechanism of ZDDP under sliding conditions in this study is attributed to tribochemical film formation on the contact surfaces. Initially, ZDDP and its solution intermediates physically or chemically adsorb onto the metal surface (Nicholls et al., 2005). Under mild friction conditions, friction pair surface mainly produces a thick phosphate film for lubrication (Kim et al., 2010). Under high sliding speed conditions, the S-P and P = S bonds are broken, and then the decomposition products containing S and P react with the friction pair surface (Xiaohong and Xuexue, 2005). This proposed mechanism is indirectly supported by the present study, where the ZDDP-containing formulations exhibited a notable reduction in COF, as shown in Figure 5, and lower WSD values compared to the base oil, as presented in Table 5.

3.3.2 Di-n-butyl-phosphite

Di-n-butyl-phosphite is a type of organophosphorus compound that has been studied for its tribological properties (Yang and Duan, 2024). It is structurally similar to other phosphite and phosphate compounds that are commonly used as lubricant additives (Shah et al., 2011). Among them, DnBP (Di-n-butyl Phosphite) exhibits unique behavior when blended with TMPTO (Trimethylolpropane Trioleate). As shown in Table 5, the concentration of DnBP significantly affects the wear scar diameter (WSD). At lower concentrations (0.6–0.9 wt. %), DnBP achieves moderate anti-wear effects with WSD values around 420–480 μm, reflecting limited surface protection. However, as the concentration increases to 1.2 wt. %, a notable improvement occurs, with the WSD dropping significantly to 325 μm.

3.3.3 Low Zinc Hydraulic Fluids Additive (HFA1)

Low-zinc lubricant additives are engineered to reduce the environmental impact and potential metal corrosion associated with traditional zinc-based additives, while maintaining effective anti-wear properties (Noria, 2024). The worn surface analysis reveals that HFA1 exhibits the largest wear scar diameter among the tested additives, with a value of 513.16 μm at 1.2% concentration.

The performance of HFA1 as a lubricant additive in comparison to raw TMPTO can be significantly influenced by various tribological factors. One primary reason for the absence of wear scar reduction with HFA1 could be its inability to form an effective tribofilm under specific test conditions such as load, temperature, or sliding speed. Tribofilms are crucial for providing surface protection, and if HFA1 does not form a robust film, it may fail to reduce wear effectively (Bachchhav et al., 2023; Wu et al., 2015).

The chemical composition and solubility of HFA1 also play a vital role in its interaction with the base oil and metal surfaces. If HFA1 has limited solubility or does not interact favorably with the base oil, it may not contribute significantly to boundary lubrication, which is essential for minimizing wear during contact between surfaces (Wu et al., 2015). This is particularly relevant in the context of TMPTO, which is known to form strong adsorption films on metal surfaces due to its polar ester functional groups (Wu et al., 2015). The polar nature of TMPTO allows it to create a protective layer that can significantly enhance its tribological performance compared to HFA1.

3.3.4 Ashless Hydraulic Fluids Additive (HFA2)

Ashless hydraulic fluids additives (HFA2) showed superior tribological properties (fricition and wear scar diameter) compared to ZDDP, DnBP and (HFA1) additives. This indicates that the presence of zinc in additives significantly influences the wear morphology on the surface (Vengudusamy et al., 2013).

The worn surface analysis of ashless hydraulic fluid additives, particularly HFA2, as shown in Figure 6, demonstrates their ability to achieve significantly smaller wear scar diameters compared to zinc-based additives like ZDDP and DnBP. For instance, HFA2 at 0.9% concentration exhibited an average wear scar diameter of 323.23 μm, significantly smaller than ZDDP at 3% (351.18 μm) and DnBP at 1.2% (325.25 μm). This data highlights HFA2's superior tribological performance, indicating that the absence of metallic elements enables smoother and more uniform tribofilm formation. This minimizes abrasive and adhesive wear, contributing to enhanced surface protection and superior performance under extreme operating conditions (Luiz & Spikes, 2020).

4.0 CONCLUSION

This work focused aimed on the comparative study of tribological performance of Trimethylolpropane Trioleate (TMPTO) formulated with various anti-wear additives, including ZDDP, DnBP, HFA1, and HFA2, against commercially available Bio VG and Mineral Oil as reference hydraulic fluids. The following conclusions can be drawn from the findings:

(1) All three hydraulic fluids (TMPTO, Bio VG and MO) show similar consistency which justifies the comparison of the tribological performance. Also, the Bio VG-based hydraulic fluids displayed better anti-wear than TMPTO and MO.
(2) The results demonstrated that TMPTO exhibited competitive wear resistance and friction-reducing properties, particularly when formulated with ashless hydraulic additives (HFA2), which achieved the smallest wear scar diameter (323.23 μm) and the lowest coefficient of friction (COF) at higher concentrations (0.9%). ZDDP and DnBP also contributed to significant improvements in tribological performance, with optimal concentrations identified at 3% and 1.2%, respectively. However, the low-zinc additive HFA1 showed limited effectiveness, especially at higher concentrations, possibly due to challenges in forming robust tribofilms.
(3) TMPTO, with its excellent tribological performance, proves to be a sustainable alternative for high-performance hydraulic fluids. Its effectiveness is further enhanced by carefully selected additives, emphasizing the need for optimized formulations to balance environmental benefits with operational efficiency.

The promising performance of TMPTO, which originates from triglycerides, highlights its potential as an eco-friendly alternative to conventional mineral-based oils for formulating innovative hydraulic fluids. The inherent polar nature of TMPTO, due to its triglyceride structure, enhances its ability to form strong boundary films, providing superior adhesion to metal surfaces and improving lubrication under extreme conditions. Additionally, the inclusion of anti-wear additives further improves its viability for high-performance applications, making it a sustainable and efficient choice for hydraulic fluid formulations.

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