

Efficient one-pot synthesis of molybdenum dialkyl dithiocarbamate and investigation on evolution mechanism of tribofilms in ester-based lubricants

Yunhan Zhang¹, Yifan Liu¹, Xianjuan Pang², Haocheng Xu³, Guangbin Yang^{1*}, Yujuan Zhang¹, Shengmao Zhang^{1*}, Pingyu Zhang¹

¹ National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng 475004, Henan, China

² National United Engineering Laboratory for Advanced Bearing Tribology, Henan University of Science and Technology, Luoyang 471023, Henan, China

³ School of Advanced Technology, Xi'an Jiaotong-Liverpool University, Suzhou 215000, Jiangsu, China

Received: August 11, 2026; Revised: September 8, 2026; Accepted: October 9, 2026

© The Author(s) 2026.

Abstract: Base oil polarity critically governs additive solubility, interfacial adsorption, and tribochemical reactions, which collectively determine friction, wear, and component service life. In this study, molybdenum dialkyldithiocarbamate (MoDTC) was synthesized via a facile one-pot route. Its dispersion stability and tribological properties were compared in two base oils with distinct polarities: polar diisooctyl sebacate (DIOS) and nonpolar polyalphaolefin (PAO6). The tribological behavior of the MoDTC/DIOS blend was further evaluated under variable applied loads and temperatures. The results reveal that MoDTC delivers superior friction-reducing and anti-wear

performance in nonpolar PAO6, attributed to stable adsorption on friction surfaces and tribochemical decomposition into protective tribofilms. In contrast, polar DIOS enables the MoDTC/DIOS blend to reach a steady friction coefficient (COF) much faster, with a drastically shortened running-in stage. Cross-sectional characterizations demonstrate that the polar DIOS environment accelerates MoDTC decomposition and rapid formation of an amorphous Mo- and S-containing tribofilm, accounting for the sharp COF decline. Nevertheless, this amorphous tribofilm exhibits low load-bearing capacity and cannot effectively suppress interfacial wear, resulting in a larger wear scar diameter (WSD) than the MoDTC/PAO6 blend. At 25 °C, MoDTC achieves optimal lubrication, reducing the COF and WSD of neat DIOS by 50.0% and 23.3%, respectively. At 75 °C, COF reduction reaches 61.5%; at 125 °C, despite severe fluctuations in the friction curve, the WSD remains smaller than that of neat DIOS, indicating sustained anti-wear capability. Combined with multiple modern characterizations, the underlying lubrication mechanisms is clarified: at low-to-medium temperatures, MoDTC preferentially generates a dense tribofilm dominated by layered MoS₂; at elevated temperatures, the tribofilm transforms into a composite of MoO₃ and MoS_xO_y. Despite increasing the COF, this composite tribofilms retain excellent load-bearing and anti-adhesion properties to mitigate severe wear. This study provides guidance for optimizing MoDTC synthesis, polarity matching, and tribofilm regulation, facilitating its wide application in lubrication systems.

Keywords: One-pot synthesis, MoDTC, Base oil polarity, Tribofilm, Tribological mechanism

*Corresponding authors: yang0378@henu.edu.cn (G. Yang); zsm@henu.edu.cn (S. Zhang)

Abstract: Base oil polarity critically governs additive solubility, interfacial adsorption, and tribochemical reactions, which collectively determine friction, wear, and component service life. In this study, molybdenum dialkyldithiocarbamate (MoDTC) was synthesized via a facile one-pot route. Its dispersion stability and tribological properties were compared in two base oils with distinct polarities: polar diisooctyl sebacate (DIOS) and nonpolar polyalphaolefin (PAO6). The tribological behavior of the MoDTC/DIOS blend was further evaluated under variable applied loads and temperatures. The results reveal that MoDTC delivers superior friction-reducing and anti-wear

performance in nonpolar PAO6, attributed to stable adsorption on friction surfaces and tribochemical decomposition into protective tribofilms. In contrast, polar DIOS enables the MoDTC/DIOS blend to reach a steady friction coefficient (COF) much faster, with a drastically shortened running-in stage. Cross-sectional characterizations demonstrate that the polar DIOS environment accelerates MoDTC decomposition and rapid formation of an amorphous Mo- and S-containing tribofilm, accounting for the sharp COF decline. Nevertheless, this amorphous tribofilm exhibits low load-bearing capacity and cannot effectively suppress interfacial wear, resulting in a larger wear scar diameter (WSD) than the MoDTC/PAO6 blend. At 25 °C, MoDTC achieves optimal lubrication, reducing the COF and WSD of neat DIOS by 50.0% and 23.3%, respectively. At 75 °C, COF reduction reaches 61.5%; at 125 °C, despite severe fluctuations in the friction curve, the WSD remains smaller than that of neat DIOS, indicating sustained anti-wear capability. Combined with multiple modern characterizations, the underlying lubrication mechanisms is clarified: at low-to-medium temperatures, MoDTC preferentially generates a dense tribofilm dominated by layered MoS₂; at elevated temperatures, the tribofilm transforms into a composite of MoO₃ and MoS_xO_y. Despite increasing the COF, this composite tribofilms retain excellent load-bearing and anti-adhesion properties to mitigate severe wear. This study provides guidance for optimizing MoDTC synthesis, polarity matching, and tribofilm regulation, facilitating its wide application in lubrication systems.

Keywords: One-pot synthesis, MoDTC, Base oil polarity, Tribofilm, Tribological mechanism

1 Introduction

Driven by the intensifying global energy crisis and increasingly stringent environmental regulations, improving energy efficiency and extending the service life of mechanical equipment has become a core research target for both academia and industry, as well as a vital pathway to fulfill the “carbon peaking and carbon neutrality” strategy [1, 2]. Lubricant additives, as core functional components regulating lubrication performance and equipment durability, play an irreplaceable role in cutting industrial energy consumption and advancing green manufacturing [3]. Statistical data indicate that advanced lubrication technologies can save 5%–15% of mechanical energy, which is of great significance for national energy security and sustainable development [4]. Therefore, developing lubricant additives integrating high-efficiency friction-reducing, anti-wear and eco-friendly properties has become a prominent research hotspot and urgent demand in tribology.

Among various lubricant additives, organomolybdenum compounds, especially molybdenum dialkyldithiocarbamate (MoDTC), have been widely adopted in industrial lubrication due to their outstanding friction-reducing capacity [5]. The core lubrication mechanism of MoDTC lies in its tribochemical reactivity under interfacial shear stress between friction pairs, which generates a layered molybdenum disulfide (MoS_2) lubricating film [6-12]. This film features ultra-low interlayer shear strength, which effectively isolates contact surfaces and markedly reduces friction coefficients to realize energy conservation. However, the tribological behavior of MoDTC is highly sensitive to service conditions, among which temperature and applied load are the two dominant parameters governing its tribochemical activity [13]. Temperature acts as the driving force for MoDTC decomposition and tribofilm formation, directly governing reaction rates and tribofilm stability; excessively high temperatures may trigger additive failure via oxidation [14]. Meanwhile, applied load determines contact zone stress states, further regulating the generation, adhesion, and delamination of MoS_2 tribofilms [15]. Existing investigations have preliminarily explored the separate effects of temperature and load on MoDTC lubrication performance, yet relevant conclusions remain inconsistent and lack systematic verification. Komaba et al. [16] performed ball-on-disk tribological tests and found that MoDTC-containing polyalphaolefin (PAO6) oil achieved the minimum friction coefficient at 80 °C. X-ray photoelectron spectroscopy (XPS) characterization confirmed that the fraction of Mo(IV) (mainly MoS_2) in the tribofilm reached 68% at this temperature, far higher than the 43% measured at 40 °C. Al Kharboutly et al. [14] verified that

100 °C is the optimal working temperature for MoDTC, where a fully formed MoS₂ delivers a friction coefficient as low as 0.063; conversely, MoDTC completely loses its lubricating efficacy at 180 °C, and tribofilms are dominated by MoO₃/FeMoO₄, leading to a sharp rise in wear volume. Garcia [17] further proposed a critical temperature threshold of approximately 90 °C for MoDTC: below this threshold, MoS₂ films dominate to maintain low friction; above this threshold, PAO base oil degradation is induced, generating amorphous carbon and elevating friction coefficients.

Regarding load effect, Fu et al. [18] reported that the friction coefficient of steel-steel contacts declined from 0.20 to 0.14 as contact pressure increased from 0.8 GPa to 1.4 GPa, proving that high contact load is a prerequisite for promoting MoS₂ film formation. On the contrary, Al Kharboutly et al [14] pointed out that MoDTC fails to sustain low-friction states when loads exceed 1.9 GPa, accompanied by a remarkable COF increment. Apart from temperature and load, MoDTC lubricating efficiency is also modulated by motion mode, base oil composition, and additive compatibility: reciprocating/rotating motion types alter tribofilm generation kinetics [19]; polar substances such as ethanol accelerate the oxidative decomposition of MoDTC, producing high-friction MoO₃ and sulfates [20]; compounding MoDTC with zinc dialkyldithiophosphate (ZDDP) or CeO₂ nanoparticles produces synergistic effect that significantly enhance load-carrying capacity and friction-reducing performance [21-25]. Nevertheless, TiO₂ nanoparticles exert antagonistic effects on MoDTC under high loads due to their abrasive polishing behavior [26].

Base oil polarity strongly affects interfacial adsorption capacity, tribofilm-forming ability, competitive adsorption with additive molecules, and tribochemical reaction pathways [27, 28]. Previous research reported that SiO₂ nanoparticles form thick deposition films in low-polarity PAO6 and medium-polarity alkyl naphthalene (AN5), yet nearly lose all friction-reducing properties in high-polar diisooctyl sebacate (DIOS) [29]. Suarez et al. [30] found that ZDDP-derived reaction films formed in nonpolar oils are thicker than those formed in polar base oils, resulting in distinct tribological performance gaps. Cen et al. [31] further confirmed that polar base oils weaken ZDDP film-forming capacity, yielding thinner reaction layers with shorter phosphate chain lengths. However, recent studies revealed variable ZDDP tribological behavior in nonpolar PAO, polar DIOS, and highly polar castor oil (CAS): the CAS system delivers lower COF, while the DIOS system exhibits optimal anti-wear performance [32]. Han et al. [33] investigated the thermal stability of dialkyldithiophosphate-modified Cu nanoparticles in base oils with different polarities and

demonstrated that the highly polar environment of DIOS generates strong electrostatic interactions with the polar terminals of nanoparticle surface modifiers, accelerating modifier desorption and triggering nanoparticle settlement and failure.

In addition, as one of the most oil-soluble high-efficiency organomolybdenum friction modifiers, the precise molecular design and optimized synthesis route of MoDTC directly determine the purity, yield, and tribological performance of final product. The molecular structure of MoDTC consists of stable coordination between one central molybdenum atom and two dialkyl dithiocarbamate ligands, forming oil-soluble complexes with unique spatial configurations and electronic properties [34]. Sakurai et al. [35] regulated product composition by introducing auxiliary sulfur sources (e.g., Na_2S) and finely tuning pH values. Tanaka et al. [36] established a multistep aqueous synthesis route, which has become a mainstream strategy to control molybdenum valence state and target product yields. This method involves stepwise addition of sulfur sources (e.g., NaHS) and reducing agents (e.g., $\text{Na}_2\text{S}_2\text{O}_4$) with distinct functions, alongside precise pH adjustment of reaction system. On the other hand, aqueous–organic phase transfer methods have been developed to improve product separation, purity, or match specific amine raw materials. A typical example is described in U.S. Patent 5494608, where core reactions proceed in the organic phase; acidification promotes phase transfer and the reaction progress, and solid products are finally obtained via washing and vacuum drying [37]. Chase et al. [38] established a synthetic route for highly sulfided molybdenum oxythiocarbamate. The prominent advantage of this route lies in its simplified reagent system, which eliminates the need for extra inorganic reagents such as sodium hydrosulfide, sulfuric acid, or hydrochloric acid. Beyond synthetic route optimization, innovative molecular design of amine raw materials to tailor the intrinsic properties of MoDTC represents another critical approach to overcome the above bottlenecks. Smith-McClain et al. [39] systematically investigated the comprehensive influences of multiple key parameters, including amine/molybdenum trioxide molar ratio, carbon disulfide dosage, diluent addition amount, reflux duration (reaction time), and reflux pressure, on final product properties. Their work quantitatively evaluated how these variables determine core performance including color, density, oil solubility, molybdenum content, sulfur content, viscosity, and S/Mo molar ratio, providing vital references for process optimization. Notably, even when CS_2 dosage deviates from theoretical stoichiometry ratios, product sulfur content remains relatively stable, highlighting the complexity of the reaction system and the

necessity of precise process control.

Based on the above research background, this work targets MoDTC and systematically evaluates its dispersion stability and tribological performance in two base oils with opposite polarity: polar DIOS and nonpolar PAO6. The influence of applied load (196~588 N) and temperature (25, 75, and 125 °C) on the tribological behavior of MoDTC/DIOS blends are explored to establish correlations between operating conditions and lubrication performance. Wear morphology, elemental distribution, and surface profiles of worn steel balls are characterized by scanning electron microscope (SEM) integrated with an energy-dispersive X-ray spectrometer (EDS), and three-dimensional profilometry. XPS is further adopted to analyze chemical composition, element valence states, and tribofilm structural evolution as a function of temperature, revealing tribofilm formation mechanism and thermal response characteristics. Overall, this study provides abundant experimental data and theoretical insight for optimizing synthesis routes, polarity matching, and lubrication mechanisms of branched alkyl MoDTC additives, supporting their widespread application in various lubrication systems.

2 Experimental

2.1 Materials

Ammonium molybdate ((NH₄)₆Mo₇O₂₄) and N,N-dimethylformamide (DMF) of analytical grade were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Diisooctylamine (analytical grade) was obtained from Aladdin Reagent (Shanghai) Co., Ltd., and carbon disulfide (analytical grade) was supplied by Shanghai Damo Chemical Reagent Co., Ltd. Industrial-grade DIOS ester base oil was provided by Qingdao Lubricating Materials Co., Ltd. Monoalkenyl polyisobutylene succinimide dispersant (RF1151) was acquired from Xinxiang Ruifeng New Materials Co., Ltd. GCr15 bearing steel balls with a diameter of 12.7 mm and Rockwell hardness of 59-64 HRC were supplied by Shanghai Steel Ball Factory. All reagents were used as received without further purification unless otherwise specified.

2.2 Synthesis and characterization of MoDTC

The target MoDTC product was synthesized via an optimized one-pot method modified from reported literature [14]. Briefly, 2.21 g (1.79 mmol) ammonium molybdate was added into a 250 mL three-neck round-bottom flask, followed by 15 mL distilled water. The mixture was magnetically stirred at room temperature until ammonium molybdate fully dissolved to form a

transparent aqueous solution. A calculated amount of diisooctylamine was dissolved in 30 mL DMF, and this solution was slowly poured into the above ammonium molybdate aqueous solution under continuous stirring for 5 min to form a homogeneous mixture.

Subsequently, the three-necked flask was immersed in an ice-water bath to maintain a constant temperature of 0–5 °C. Excess carbon disulfide was dropwise added into the reaction system under magnetic stirring. During dropwise addition, the solution gradually turned into a purple suspension. After complete CS₂ addition, the reaction was maintained in the ice-water bath for an additional 30 min. The reaction system was then transferred to an oil bath, heated to 105 °C, and held at constant temperature for 3 h until the solution fully changed from purple to bright green.

After the reaction finished, the mixture was cooled to room temperature. The crude product was sequentially subjected to extraction, washing, filtration, rotary evaporation, and vacuum drying at 60 °C for 4 h to obtain a green viscous MoDTC product. The synthetic route and chemical structure of MoDTC are illustrated in Fig. 1. This preparation procedure is simple with a limited variety of reagents employed.

Fig. 1 Schematic diagram of the synthesis process and chemical structure of MoDTC.

Fourier transform infrared (FTIR) spectra of the as-prepared MoDTC were recorded on a Bruker Vertex 70 spectrometer (Bruker Corporation, USA) over the wavenumber range of 400–4000 cm⁻¹ to identify molecular chemical structures.

Thermogravimetric analysis (TGA) was performed on a TGA/DSC3+ simultaneous thermal analyzer (Mettler Toledo, Switzerland) to evaluate the thermal stability of MoDTC. The tests were carried out under a nitrogen atmosphere with a heating rate of 10 °C/min, over a temperature range from room temperature to 800 °C.

The oxidation stability of neat DIOS, neat PAO6, and their blends containing 1.0 wt.% MoDTC was measured on a DSC 204 HP high-temperature differential scanning calorimeter (NETZSCH, Germany) under air atmosphere with a heating rate of 10 °C/min from room temperature to 300 °C. Kinematic viscosity and density of DIOS, PAO6, MoDTC/DIOS, and MoDTC/PAO6 blends were measured using an SVM™ 3001 Stabinger viscometer densimeter (Anton Paar, Austria). Densities were calculated based on kinematic viscosities measured at 40 °C and 100 °C; detailed results are listed in Table. S1. The results indicate that the adding of MoDTC has little effect on the inherent

physicochemical properties of the base oils, with only minor variations observed.

2.3 Tribological performance testing

2.3.1 Effect of base oil polarity on MoDTC tribological properties

A series of MoDTC/DIOS and MoDTC/PAO6 blends were prepared by dispersing MoDTC additives into DIOS and PAO6 base oil at different mass fractions. Tribological measurements were carried out on an MS-10J four-ball tribotester (Jinan Chenda Testing Machine Co., Ltd., China) using GCr15 bearing steel balls as friction pairs.

Tribological tests were conducted under an applied load of 392 N, rotational speed of 1200 rev/min, and temperature of 75 °C for 60 min, following the Chinese petrochemical industry standard NB/SH/T 0189-2017. Each test was repeated three times to reduce experimental errors, and COF-time curves were automatically recorded by the testing system. After each test, the wear scar diameters (WSD) of the three lower steel balls were measured using an optical microscope equipped with a charge-coupled device (CCD), and the average WSD was adopted as the core indicator to evaluate anti-wear performance.

2.3.2 Effects of load and temperature on tribological performance

To explore the load dependence of tribological behavior, tribological tests of 1.0 wt.% MoDTC/DIOS blend were performed at room temperature (25 °C) and a rotating speed of 1200 rev/min for 60 min. Applied loads were adjusted from 196 N to 588 N with an interval of 98 N (196, 294, 392, 490, and 588 N).

To investigate temperature effects on tribological performance, tribological evaluations of the 1.0 wt.% MoDTC/DIOS blend were carried out at a fixed applied load of 392 N and rotational speed of 1200 rev/min for 60 min, with test temperature controlled at 25, 75, and 125°C.

2.3.3 Wear surface characterization

After tribological testing, friction pairs were disassembled. Lower steel balls were ultrasonically cleaned with petroleum ether (boiling range: 60–90 °C) three times (5 min per cycle) to remove residual lubricant and wear debris, followed by air-drying at room temperature for subsequent characterization.

A Bruker Contour GT-K white light interferometer (Bruker, Germany) was used to observe three-dimensional (3D) wear scar topography and two-dimensional (2D) profile curves, as well as to calculate wear scar depth and wear volume.

A scanning electron microscope (SEM, Carl Zeiss, Germany) coupled with an energy-dispersive spectrometer (EDS) was utilized to characterize micromorphologies of worn surfaces. EDS analysis was conducted to determine the elemental composition and distribution of tribofilms formed on wear scar.

X-ray photoelectron spectroscopy (XPS, Axis Ultra, Kratos, UK) was adopted to analyze chemical states (valence states of Mo, S, C, and O) of characteristic elements in tribofilms, aiming to elucidate tribofilm formation and evolution mechanisms.

Tribofilm cross-sections of steel balls tested with MoDTC/DIOS blend at 75 °C and 392 N were fabricated via focused ion beam (FIB, FEI Helios Nanolab600i, USA) system, and microstructures were observed under a transmission electron microscope (TEM, FEI Tecnai G2 F30, USA).

2.4 Adsorption performance test

A dissipation-mode quartz crystal microbalance (QCM-D) was used to investigate the adsorption behaviors of neat DIOS and 1.0 wt.% MoDTC/DIOS blend on gold-coated quartz crystal sensors at different temperatures, revealing MoDTC adsorption patterns on metal surfaces and temperature-dependent adsorption rules.

The detailed testing procedure is described as follows: (1) Dodecane was pumped into the QCM-D flow cell at 40 µL/min until frequency (f) and energy dissipation factor (ΔD) baselines stabilized, serving as blank reference. (2) The fluid was switched to neat DIOS while maintaining a flow rate of 40 µL/min; adsorption proceeded for 40 min, with real-time recording of f and ΔD variations. (3) The fluid was replaced with 1.0 wt.% MoDTC/DIOS blend, and pumping continued until adsorption equilibrium was achieved before terminating the adsorption test. (4) Finally, petroleum ether was circulated through the flow cell and pipelines to clean the system until signals returned to stable baselines, followed by purging and drying with high-purity N₂ to complete one test cycle.

The mass variation of adsorbed film was calculated using the Sauerbrey equation:

$$\Delta m_f = \frac{\rho_q h_q}{f_0} \times \frac{\Delta f}{n} = -C \Delta f \quad (1)$$

where ρ_q is the density of quartz crystal (2648 kg/m³), h_q is quartz crystal thickness, f_0 is the fundamental resonance frequency of quartz crystal (5 MHz), n is overtone number, and C is the Sauerbrey constant (17.7 ng/(cm²·Hz)). Adsorbed film mass variations were calculated from frequency shift (Δf). Combined with dissipation factor (ΔD) changes, the structural compactness

and viscoelastic properties of adsorbed film were analyzed to clarify MoDTC adsorption mechanisms on metal substrates

3 Results and discussion

3.1 Characterization of synthesized MoDTC

Fig. 2(a) presents the FTIR spectrum of as-synthesized MoDTC. The absorption peaks at 2962 cm^{-1} and 2931 cm^{-1} correspond to asymmetric stretching vibrations of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$) groups, respectively. The peak at 2869 cm^{-1} is assigned to symmetric $-\text{CH}_3$ stretching vibration, while characteristic signals at 1380 cm^{-1} and 1446 cm^{-1} originate from bending vibrations of $-\text{CH}_3$ and $-\text{CH}_2$ moieties. The detection of these alkyl-related absorption bands confirms that long alkyl chains derived from dialkylamine were successfully introduced into the MoDTC molecular framework.

Moreover, the absorption peak at 1143 cm^{-1} reflects C–N stretching vibration; strong absorption bands at 1519 cm^{-1} and 1232 cm^{-1} are characteristic C=S stretching vibrations of the N–C(S)–S functional group. The distinct peak at 972 cm^{-1} is attributed to Mo=O stretching modes, and the signal at 474 cm^{-1} acts as a fingerprint peak for Mo–S heterocyclic structures. These spectral features collectively verify that sulfur atoms form stable coordination bonds with central molybdenum atom, and the synthesized product possesses the characteristic chelated or sulfur-bridged tetranuclear structure of MoDTC, confirming successful preparation of the target compound. Fig. 2(b) shows the TGA curve of MoDTC, revealing two distinct thermal decomposition stages. The initial decomposition temperature of the first stage is $204.9\text{ }^{\circ}\text{C}$, corresponding to the cleavage of labile organic moieties in MoDTC molecules, including thiocarbamate groups and Mo–S heterocyclic rings. The second decomposition stage exhibits a weight loss rate of 49.33%, mainly induced by thermal cracking of long alkyl side chains. After complete thermal decomposition, the residual mass fraction reaches approximately 30%, which is inferred to consist of molybdenum sulfides and oxides (MoS_2 and MoO_3). Notably, the temperature corresponding to 50% weight loss of MoDTC reaches $331\text{ }^{\circ}\text{C}$, demonstrating excellent thermal stability that satisfies the application demands of ester lubricants under medium-to-high temperature operating conditions.

Fig. 2 (a) FT-IR spectrum of MoDTC, (b) TGA curve of MoDTC.

MoDTC additive was separately blended into PAO6 and DIOS base oils at a concentration of 1.0

wt.%. All mixtures were ultrasonicated for 30 min to achieve homogeneous dispersion. As shown in Fig. 3, MoDTC can be stably dispersed in polar DIOS without obvious sedimentation even after 30 days of static storage. Unlike MoDTC in polar DIOS, which disperses stably without any dispersant additive, MoDTC shows poor dispersibility in neat PAO6 and readily sediments. When blended with RF1151 dispersant exhibits no significant sedimentation and maintains uniform dispersion. This phenomenon proves that RF1151 dispersant endows MoDTC with favorable dispersion stability in nonpolar PAO6 base oil. In addition, MoDTC exhibits a certain antioxidant capacity in both PAO and DIOS base oils and elevates the oxidation onset temperatures of the two base oils (Fig. S1).

Fig. 3 Optical photographs of static sedimentation tests for MoDTC in two base oils: (a) PAO6, (b) DIOS.

3.2 Tribological performance

3.2.1 Effect of base oil polarity on MoDTC tribological properties

Firstly, the influence of MoDTC concentration on the tribological performances of DIOS base oil was investigated. As illustrated in Fig. 4(a), adding MoDTC significantly reduces the COF of DIOS, which originates from complex tribochemical reactions of MoDTC that generate thin, robust MoS₂ tribofilms on friction pair surfaces under shear stress. As MoDTC concentration increases, the COF gradually declines and friction curves stabilize in the later stage when the concentration exceeds 0.4 wt.%. This trend is attributed to improved tribofilm coverage: higher MoDTC dosages promote more complete surface coverage by MoS₂ films and stabilize COF. However, concentrations above 1.0 wt.% induce obvious friction curves fluctuations, which likely arise from intensified competitive adsorption between excessive MoDTC and polar DIOS ester molecules, forming non-uniform, loosely bound surface film. As shown in average COF and WSD histograms (Figs. 4b and 4c), both COF and WSD of DIOS blends decline significantly after MoDTC addition. Average COF and WSD decrease with increasing additive concentration, reaching the minimum COF at 1.0 wt.% MoDTC. Although further increasing the additive dosage slightly reduces WSD, it destabilizes friction curves and elevates average COF. Therefore, 1.0 wt.% is identified as the optimal MoDTC concentration, which reduces average COF and WSD by 61.54% and 26.84%, respectively, compared with neat DIOS.

Fig. 4 Tribological performance of MoDTC in DIOS base oil: (a) time-dependent COF curves, (b) average COF versus additive concentration, (c) variation of WSD with additive concentration.

Fig. 5 presents COF versus time curves and WSD distributions of PAO6 blends with different MoDTC mass fractions. Neat PAO6 delivers a relatively low initial COF, yet friction curves gradually rise stabilize at approximately 0.095 as testing proceeds. After MoDTC incorporation, all friction curves lie below that of neat PAO6 and stabilize after a certain running-in period. With increasing additive concentration, COF and WSD first decrease and then increase. At 0.8 wt.% MoDTC, the terminal COF reaches 0.035, accompanied by a minimum WSD of 0.411 mm. Relative to neat PAO6, the COF and WSD decrease by 63.16% and 45.13%, respectively, verifying that MoDTC significantly improves friction-reducing and anti-wear performance. To eliminate potential interference of the dispersant RF1151 on PAO6 tribological properties, 0.4 wt.% RF1151 (consistent with the mass ratio of MoDTC to dispersant 1:1 at the optimal MoDTC concentration of 0.8 wt.%) was added into neat PAO6. As indicated by COF–time curves in Fig. 5a, RF1151 cannot improve PAO6 lubrication performance and even increases COF. Therefore, the enhanced friction-reducing capacity of MoDTC-containing PAO6 blends originates exclusively from MoDTC rather than RF1151, which only functions as a dispersant.

Fig. 5 Tribological performance of MoDTC in PAO6 base oil: (a) time-dependent COF curves, (b) WSD as a function of additive concentration.

Comparisons of Figs. 4 and 5 reveals distinct differences in friction curves characteristics of MoDTC/PAO6 and MoDTC/DIOS blends at their respective optimal additive concentrations. For the MoDTC/DIOS system, COF drops rapidly at the initial test stage and enters a stable phase after roughly 1200 s, with steady COF maintained near 0.045. In contrast, the PAO6 system requires a much longer running-in period, and COF stabilizes at approximately 0.040 only in the later test stage. Further WSD comparisons show that MoDTC-containing PAO6 delivers smaller WSD values than the MoDTC/DIOS system. This observation demonstrates that base oil polarity plays a dominant role in tribochemical film formation rates of MoDTC. Polar ester DIOS molecules readily adsorb onto metal surfaces and compete with MoDTC, hindering continuous tribofilm growth and yielding a smaller WSD reduction ratio (25.61%) than nonpolar PAO6 (45.33%). In contrast,

nonpolar PAO6 exhibits weaker interfacial adsorption capacity, allowing MoDTC molecules to accumulate readily at contact surface [40]. Recent studies further support this polarity-dependent behavior. For instance, Chen et al. [41] reported that Ag/2D Ni-MOF nanohybrids in highly polar castor oil exhibited distinct tribological performance compared with nonpolar systems, emphasizing that base oil polarity is a critical factor governing additive dispersion, interfacial adsorption, and tribofilm formation.

Figs. S2 and 6 display 3D morphologies, SEM images, and element mappings of worn steel ball surfaces lubricated by DIOS and PAO6 blends with optimal MoDTC concentrations. Steel balls lubricated by neat base oils possess large WSD values, with obvious pits and plowing grooves on worn surfaces. After adding MoDTC, wear scar depth and WSD decrease remarkably. Further comparative analysis indicates that MoDTC/PAO6 system generates smaller, smoother wear scars, while worn surfaces of the MoDTC/DIOS system still contain pits, revealing inferior anti-wear performance relative to MoDTC/PAO6. Elemental mapping results confirm enrichment of Mo and S elements on steel ball surfaces for both blends, verifying tribofilm formation.

Fig. 6 SEM images and corresponding EDS elemental mapping of wear scar on steel balls lubricated by (a1) neat DIOS, (b1) 1.0 wt.% MoDTC/DIOS, (a2) neat PAO6, and (b2) 0.8 wt.% MoDTC/PAO6.

High-magnification SEM observations of wear scar micro-details are shown in Fig. 7. The worn surface of the MoDTC/DIOS system is covered with abundant flat, patch-like smooth tribofilms, whereas the MoDTC/PAO6 system exhibits more sliding-direction wear tracks with only sparse patch-like tribofilms scattered in local regions. The corresponding EDS spectra further provided direct evidence for the distribution of these tribofilms.

Fig. 7 High-magnification SEM images and local EDS spectra of wear scar on steel balls: (a) 1.0 wt.% MoDTC/DIOS; (b) 0.8 wt.% MoDTC/PAO6.

3.2.2 Effect of load on MoDTC tribological properties

To investigate the load-dependent lubrication enhancement of MoDTC, this work systematically evaluated the tribological behaviors of neat DIOS and 1.0 wt.% MoDTC/DIOS blend. Figs. S3 and 8 present the COF-time curves of GCr15 steel balls lubricated by both systems under load ranging from 196 N to 588 N, alongside average COF and WSD variations.

For neat DIOS, COF first rises and then declines with increasing load, peaking at 0.130 at 294 N; COF gradually decreases as load further increase beyond this point. In contrast, MoDTC-containing lubricants exhibit a distinct COF variation pattern tightly correlated with tribofilm generation, stability, and failure. Under low loads (≤ 294 N), insufficient contact pressure fails to drive adequate interfacial adsorption of MoDTC molecules and intensive tribochemical reactions, producing incomplete, discontinuous lubricating film. This leads to high proportions of direct asperity contact and relatively high COF values.

When the applied load increased to 392 N, interfacial adsorption and tribochemical reaction of MoDTC reach optimal states, generating dense, intact protective lubricating film with appropriate thickness. Such films effectively isolate friction surfaces and minimize direct asperity contact, achieving the minimum COF. Further load elevation (490–588 N) induces contact pressure exceeding the load-bearing capacity of tribofilms, triggering local film rupture and extrusion. Meanwhile, high loads cause severe elastoplastic deformation of friction surfaces and increased surface roughness, ultimately leading to COF rebound. Quantitative analysis confirms the superior friction-reducing capacity of MoDTC: relative to neat DIOS, the 1.0 wt.% MoDTC/DIOS blend reduces COF by 37.9 %, 46.1 %, 50.0 %, 35.9 %, and 37.0 % at 196, 294, 392, 490, and 588 N, respectively, maintaining effective friction-reducing performance across the entire tested load range.

Fig. 8 Tribological performance of 1.0 wt.% MoDTC/DIOS blend under varying applied loads: (a) average COF at different loads, (b) WSD at different loads.

The WSD of steel balls under both lubrication systems consistently increases with rising load (Fig. 8b), originating from intensified contact pressure that aggravates surface asperity stress, elastoplastic deformation, and surface damage. Hard surface asperities are more likely to plow deeper and wider grooves under high loads, further expanding wear scar sizes, and the 3D wear scar morphologies (Fig. S4) visually verify the anti-wear enhancement of MoDTC. Notably, MoDTC effectively suppresses WSD expansion: at the five tested load levels, WSD values of steel balls lubricated by MoDTC/DIOS blends decrease by 19.1%, 23.3%, 26.6%, 27.4%, and 39.7%, respectively, compared with neat DIOS. It is worth noting that the WSD at 588 N is slightly lower than that at 490 N, accompanied by a minor reduction in the COF. This demonstrates that the COF reduction is not caused by lowered Hertzian contact stress stemming from wear-scar enlargement.

It is speculated that elevated contact stress accelerates MoDTC decomposition and promotes tribofilm generation.

This remarkable anti-wear effect mainly stems from the tribochemical decomposition of MoDTC during friction, generating MoS₂-dominated reactive lubricating films. The layered crystal structure of MoS₂ features weak van der Waals forces between adjacent layers, facilitates interlayer sliding to realize simultaneous friction-reducing and anti-wear effects. Furthermore, this reactive film uniformly covers friction surfaces, fills micro-pits and surface defects, improves surface smoothness, and weakens mechanical interactions between asperities to minimize wear scar size. Nevertheless, excessive pressure under high load induces local film rupture, expanding contact areas and accelerating wear. In addition, frictional heat generated at high loads elevates friction surface temperatures, reducing material hardness and strength and further accelerating WSD growth.

Fig. 9 SEM images and corresponding EDS elemental mapping of wear scar lubricated by (a) neat DIOS, (b) 1.0 wt.% MoDTC/DIOS under applied loads of (1) 196 N, (2) 294 N, (3) 392 N, (4) 490 N, and (5) 588 N.

SEM and EDS characterizations (Fig. 9) further clarify wear mechanisms and tribofilm formation rules. Consistent with WSD trends, wear scar sizes expand with increasing load for both lubrication systems, accompanied by elevated wear volumes. For neat DIOS, only C and O elements are detected on worn surfaces, indicating severe oxidative wear as the dominant surface damage pathway. In contrast, the MoDTC/DIOS system exhibits obvious enrichment of Mo and S elements alongside C and O on wear scars, confirming that MoDTC generates Mo/S-rich tribofilms on friction pair surfaces to deliver excellent tribological performance. Even when applied loads exceed tribofilm load-carrying capacity and trigger local rupture, persistent enrichment of Mo and S elements still effectively mitigates wear severity. Consequently, wear degrees of steel balls lubricated by MoDTC/DIOS remain significantly lower than those under neat DIOS lubrication.

3.2.3 Effect of test temperature on MoDTC tribological properties

Tribological measurements of neat DIOS and 1.0 wt.% MoDTC/DIOS blend were performed over a temperature range of 25–125 °C. Combined with surface morphology, elemental composition, and tribofilm evolution behavior, temperature-dependent lubrication mechanisms were analyzed. COF variation curves (Fig. S5a–c) reveal distinct temperature-induced differences between the two

lubrication systems. At 25 °C (Fig. S5a), neat DIOS exhibits high initial friction coefficient that briefly decline before rising and stabilizing; by contrast, MoDTC/DIOS blends deliver much lower initial COF and maintain stable signal with minor fluctuations throughout testing, proving stable tribofilm formation even at room temperature. At 75 °C (Fig. S5b), neat DIOS displays severe COF fluctuations, while MoDTC enables the blend to retain low, stable COF with prominent friction-reducing effects. At 125 °C (Fig. S5c), the significantly reduced viscosity of neat DIOS leads to oil film thinning and a shift toward more severe boundary lubrication. The initial transient COF drop may result from thermal softening of surface asperities, while the subsequent sustained fluctuations reflect the failure of physically adsorbed boundary films under elevated temperature and shear. Conversely, the MoDTC/DIOS system exhibits “early-stage effective, late-stage deterioration” behavior: COF remains low initial stage yet rises sharply in the later test period, eventually exceeding that of neat DIOS. This phenomenon originates from two key factors: first, MoS₂ generated by MoDTC decomposition is susceptible to oxidation into poorly lubricative MoO₃ under high-temperature oxidative environments; second, elevated temperatures accelerate MoDTC decomposition and hinder continuous formation of stable effective tribofilms on friction pair surfaces [42]. Relative to neat DIOS, MoDTC reduces average COF by 50.0% and 61.54% at 25 °C and 75 °C, respectively (Fig. 10a), demonstrating that MoDTC provides reliable lubrication protection for DIOS base oil over a wide temperature window.

In terms of anti-wear performance (Fig. 10b), the MoDTC/DIOS system delivers smaller WSD values than neat DIOS across all tested temperatures, with WSD reductions of 29.0%, 39.3%, and 34.8% at 25, 75, and 125 °C, respectively, verifying that MoDTC effectively improves the anti-wear capacity of DIOS. For neat DIOS, WSD changes slightly between 25 °C and 75 °C; at 125 °C, drastic viscosity reduction induces severe thinning or failure of oil films, placing friction pair under oil-starved conditions or direct metal-metal contact. This triggers severe adhesive and abrasive wear, resulting in a sharp WSD increment [43-45].

Fig. 10 Tribological performance of neat DIOS and MoDTC/DIOS blends at different temperatures, (a) average COF and (b) WSD.

3D wear scar morphologies, 2D profile curves (Fig. S6) and SEM-EDS results (Fig. 11) clarify temperature influences on tribofilm evolution and wear mechanisms. Across the entire temperature

range, temperature exerts a significant regulatory effect on the tribological properties of lubrication systems, and the wear volume generally increases with the rise of test temperature. At 125 °C, neat DIOS generates severe wear scratches and deep grooves on worn surface, which originates from the physical adsorption nature of its lubricating films. Boundary films formed via weak intermolecular forces readily desorb and fail under localized high pressure, elevated temperature, and shear stress during friction, leading to direct metal contact and severe wear.

For the MoDTC/DIOS system, although WSD expands as test temperatures rises from low to medium levels, it remains markedly smaller than that of neat DIOS with much shallower wear depth. MoDTC forms chemically bonded solid lubricating film on substrate surface via tribochemical reactions, combining low shear strength with high load-bearing capacity to effectively isolate and protect friction surfaces. At 75 °C, worn surfaces of the MoDTC/DIOS system appear smooth and flat with shallow grooves, which originates from uniform, robust protective tribofilms consistent with the optimal tribological performance measured at this temperature. At 125 °C, worn surface became rough and uneven with increased depth, and the dominant wear mechanism shifts from mild tribochemical wear to severe abrasive and fatigue wear, directly causing elevated, fluctuating friction coefficient.

Fig. 11 SEM images and EDS elemental mappings of wear scar surfaces on steel balls lubricated with (a) DIOS and (b) 1.0 wt.% MoDTC/DIOS at (1) 25 °C, (2) 75 °C, (3) 125 °C.

EDS analysis reveals that only C and O signals are detected on wear surface lubricated by neat DIOS at 75 °C without Mo or S characteristic peaks. In contrast, obvious Mo and S enrichment is observed on worn surfaces of the MoDTC/DIOS system, preliminarily confirming the formation of Mo/S-containing tribochemical reaction films. When temperature rises to 125 °C, elevated O signal intensity indicates synchronous generation of MoO_3 . Although MoO_3 tends to increase the friction coefficient, its rigid film structure effectively blocks direct metal–metal contact and mitigates wear severity, verifying that MoDTC sustains anti-wear capacity across a wide temperature range.

3.3 Adsorption behavior

To reveal the intrinsic lubricating mechanism of MoDTC in ester lubricants, QCM-D technology was adopted to systematically investigate adsorption behavior of 1.0 wt.% MoDTC/DIOS blend on gold-coated sensor surface at variable temperatures. Fig. 12 presents time-dependent frequency

shift, energy dissipation factor, adsorbed film thickness, and deposited mass on gold-coated sensors surface at 75 °C and 125 °C. The entire testing procedure is divided into three distinct stages: the pink region represents n-dodecane injection for initial baseline establishment; the yellow region corresponds to DIOS infusion to build secondary baselines; the subsequent stage conducts formal adsorption experiment using MoDTC/DIOS blends.

Fig. 12 Adsorption behavior of MoDTC on gold-coated quartz crystal sensors at 75 °C and 125 °C, (a) frequency shift, (b) energy dissipation factor, (c) adsorbed film thickness, (d) deposited mass.

At 75 °C, polar ester functional groups in DIOS molecules form structurally stable, well-ordered physically adsorbed boundary film on metal surfaces. These adsorbed films act as a physical barrier to prevent direct contact between mating metal surfaces, providing fundamental lubrication protection for tribological systems. High temperatures reduce base oil viscosity and thin the oil film, shifting the lubrication regime toward more severe boundary lubrication. For neat DIOS, this viscosity reduction contributes to the destabilization of physically adsorbed boundary films and subsequent lubrication degradation [46].

For MoDTC/DIOS blends, adsorption frequency at 75 °C is substantially higher than that at 125 °C, accompanied by markedly thicker adsorbed films at 75 °C. These observations demonstrate that MoDTC can form dense, effective adsorption layers on metal surfaces under relatively low-temperature conditions. In contrast, at 125 °C, thermal oxidative decomposition products of DIOS compete with MoDTC molecules for active metal surface adsorption sites, hindering continuous formation of effective MoDTC lubricating films. In terms of adsorbed film structural characteristics, data in Fig. 12(c) indicate that MoDTC adsorption layer reach approximately 2 nm in thickness, characteristic of dense monolayer adsorption of small organic molecules. Furthermore, as shown in Fig. 12(b), the energy dissipation factor of MoDTC adsorbed film exceeds 1×10^{-6} , revealing that MoDTC forms viscoelastic adsorption layer on metal surfaces. The viscoelastic properties combined with dense monolayer structures account for temperature-dependent differences in MoDTC lubrication performance.

3.4 Lubrication mechanism

3.4.1 Lubrication mechanism of MoDTC in base oils with different polarities

To clarify chemical compositions and valence states of tribofilms generated by MoDTC in base oils

with different polarities, XPS characterization was performed on worn surfaces lubricated by MoDTC/DIOS and MoDTC/PAO6 blends. As shown in Fig. 13, Mo, O, S, C, and Fe elements were detected on worn surfaces of both lubrication systems. For MoDTC/DIOS, characteristic doublet peaks at 228.49 eV, 231.54 eV and 232.56 eV, 235.61 eV (Fig. 13b) are assigned to Mo^{4+} and Mo^{6+} species, respectively. Combined with S 2*p* characteristic peaks at 161.77 eV and 163.07 eV (Fig. 13d) and O 1*s* signals at 530.6 eV (Fig. 13c), it is confirmed that MoO_3 and MoS_2 components form on wear scar surface [47, 48]. Similarly, Mo^{4+} and Mo^{6+} characteristic peaks at 227.50 eV, 230.85 eV and 232.62 eV, 235.91 eV (Fig. 13b) were observed for the MoDTC/PAO6 system. Combined with O 1*s* (530.28 eV) and S 2*p* (162.0 eV, 163.1 eV) peaks, tribofilms containing MoS_2 and MoO_3 was also formed on friction surfaces. Moreover, peak area integration comparisons reveal that the MoS_2 proportion in the DIOS system is significantly higher than that in the PAO6 system, indicating accelerated MoS_2 generation in polar ester DIOS environments. C 1*s* spectra (Figs. 13e) exhibit characteristic peaks near 284.8 eV, 286.0 eV, and 288.0 eV, corresponding to C–C, C–O, and C=O bonds, respectively, confirming thermal oxidative decomposition of base oils during friction. In addition, characteristic peaks ranging from 709.40 to 710.62 eV, 711.50 to 712.47 eV, and near 714.2 eV are assigned to ferrous oxide (FeO), ferric oxide (Fe_2O_3), and ferrous sulfate (FeSO_4), respectively; peaks at 168.0 eV and 169.0 eV correspond to SO_4^{2-} species, further verifying oxidation and sulfidation reactions in friction contact zones under high temperature and pressure [49].

Fig. 13 XPS spectra of worn steel ball surfaces lubricated by the 1.0 wt.% MoDTC/DIOS (upper panel) and 0.8 wt.% MoDTC/PAO6 blends (lower panel) (four-ball test: 75 °C, 392 N, 3600 s). Tribofilm cross-sectional lamellae were fabricated via FIB and characterized by TEM. As shown in Fig. 14, elemental mapping and line scanning profiles reveal uniform distribution of characteristic Mo and S elements within tribofilms, consistent with MoS_2 components identified via XPS. Extensive literature reports that MoDTC in PAO base oils forms layered crystalline MoS_2 tribofilms with thickness generally below 100 nm [50]. However, in polar DIOS base oil, MoDTC fails to generate layered crystalline MoS_2 structure (Fig. 15). Instead, tribofilms grow to 300–500 nm in thickness, with only sparse randomly distributed spherical low-contrast crystalline phases embedded inside (Fig. 15b). Lattice fringe measurement and diffraction pattern indexing identify

these phases as FeO crystals (Figs. 15c, d). The FeO crystallites originated from the oxidation of the GCr15 steel substrate under the severe contact conditions. As stress concentrators, they can disrupt the amorphous film and reduce its load-bearing capacity, thereby increasing the WSD in the DIOS system. These observations indicate that friction reduction of MoDTC in polar ester DIOS cannot be attributed to intralayer sliding of layered MoS₂ crystals. Previous research reported that highly polar environments strengthen electrostatic interactions between base oil molecules and additives, potentially accelerating additive decomposition [33]. This implies that MoDTC in DIOS may partially decompose driven by the polar base oil prior to tribochemical reactions, generating amorphous MoS₂ deposited films on friction surfaces. Under continuous shear stress, film surfaces gradually transform into crystalline MoS₂ to deliver friction-reducing capacity. This interpretation aligns with earlier friction tests results: MoDTC in polar system rapidly reduces COF to stable minimum values (Fig. 4a), whereas nonpolar PAO6 systems require much longer friction induction period (Fig. 5a). Such differences are consistent with accelerated MoDTC decomposition in highly polar environment.

Fig. 14 (a)TEM images and EDS elemental mapping of wear scar cross-sections, (b) line scanning of major elements within the tribofilm formed on steel ball surfaces lubricated by 1.0 wt.% MoDTC/DIOS blends.

Fig. 15 (a) cross-sectional bright-field TEM image, (b) high-magnification TEM image of a randomly selected local region, (c) HRTEM lattice fringe image, and (d) corresponding fast Fourier transform diffraction pattern of the tribofilm formed on steel balls lubricated with 1.0 wt.% MoDTC/DIOS.

The influence of base oil polarity on MoDTC lubrication mechanism is schematically illustrated in Fig. 16. Polar ester functional groups in DIOS form coordination bonds and hydrogen bonds with active metal surface sites, hindering effective adsorption of weakly polar additives and weakening their friction-reducing and anti-wear performance. Nevertheless, MoDTC itself contains strongly polar dithiocarbamate groups, enabling competitive adsorption with DIOS molecules to improve interfacial coverage. Meanwhile, at the initial friction stage, highly polar DIOS accelerates MoDTC decomposition to form amorphous MoS₂ film, drastically shortening running-in periods. In addition, physically adsorbed DIOS films facilitate ordered deposition of MoS₂ and other reaction products,

generating continuous, dense Mo/S-enriched composite tribofilms.

In contrast, in nonpolar PAO, MoDTC preferentially binds to active sites on metal friction pair surfaces, with nonpolar alkyl chains extending outward to form oriented adsorption layers. In this case, additive decomposition fully relies on localized high temperature and pressure generated by frictional shear, leading to relatively slow tribofilm formation. Furthermore, decomposition products grow directly on metal surface and tend to form discontinuous, poorly adherent tribofilms.

Fig. 16 Schematic illustration of MoDTC lubrication mechanisms in nonpolar PAO6 and polar DIOS ester base oils.

3.4.2 Temperature-dependent lubrication mechanism of MoDTC

To further reveal temperature-dependent lubrication mechanism of MoDTC, XPS characterizations were conducted on worn steel ball surfaces lubricated by MoDTC/DIOS blend at 75 °C and 125 °C. High-resolution fitting curves of Mo 3d, O 1s, S 2p, C 1s and Fe 2p core-level spectra are displayed in Fig. 17. At 75 °C, Mo 3d characteristic peaks at 228.49 eV and 231.54 eV correspond to Mo⁴⁺ species, while signals at 232.56 eV and 235.61 eV are assigned to Mo⁶⁺. Combined with O 1s and S 2p spectra features, it can be inferred that molybdenum-based compounds (MoS₂ and MoO₃) formed on worn steel ball surface. In C 1s spectra, characteristic peaks at 284.8 eV and 286.64 eV originate from C—C and C—O bonds, respectively. The C 1s peak at 288.19 eV paired with the O 1s signal at 533.76 eV confirms C=O bonds derived from DIOS ester groups or their oxidation products. Fe 2p spectra exhibit characteristic peaks at 709.48 eV, 711.59 eV, and 714.21 eV, indicating formation of iron oxides and sulfides (FeO, Fe₂O₃, FeSO₄) on worn surfaces. This result proves that oxidation and sulfidation reactions occur on iron substrates within friction contact zone during tribological processes.

Fig. 17 XPS spectra of the wear scar surface on steel balls lubricated with by 1.0 wt.% MoDTC/DIOS at 75 °C (upper panel) and 125 °C (lower panel) (four-ball test: 392 N, 3600 s). When temperature rises to 125 °C, Mo 3d spectra display characteristic signals of molybdenum oxidsulfide (MoS_xO_y) at 229.61 eV and 232.66 eV, while peaks at 232.18 eV and 235.23 eV still correspond to Mo⁶⁺ species. Combined with the O 1s peak at 531.97 eV, MoO₃ formation is further verified. Compared with test results at 75 °C, the contents of MoO₃ and MoS_xO_y on worn surface at

125 °C are markedly higher than MoS₂ fractions. Elevated proportions of these molybdenum oxides/oxyulfides account for experimental observations of late-stage COF fluctuations and growth under 125 °C conditions. In addition, Fe 2*p* spectra at 125 °C still detect characteristic peaks of FeO, Fe₂O₃, and FeSO₄, indicating persistent substrate oxidation and sulfidation even at high temperatures. The above XPS results demonstrate that MoDTC undergoes oxidative decomposition under high-temperature environments. The dominant tribofilm components shift from MoS₂ at low-to-moderate temperatures to MoO₃ and MoS_xO_y at elevated temperatures. These molybdenum oxides and oxyulfides deliver inferior friction-reducing performance relative to layered MoS₂, leading to significant deterioration of MoDTC friction-reducing capacity at high temperatures.

The temperature-dependent lubrication mechanism of MoDTC additive in DIOS ester oil is schematically presented in Fig. 18. At a moderate temperature of 75 °C, polar ester groups of DIOS rapidly adsorb onto gold-plated/steel interfaces to form structurally stable physical boundary films that provide basic separation between metal counterparts. MoDTC molecules further adsorb on the outer layer of ester films, forming dense viscoelastic monolayers with thickness of approximately 2 nm. The high energy dissipation factor of these monolayers endows adsorbed films with excellent deformation adaptability to buffer initial frictional impacts. Upon entering friction contact stages, frictional shear stress and mild interfacial temperature elevation trigger controlled MoDTC decomposition. Released active Mo and S atoms undergo tribochemical reactions with Fe atoms from steel substrates, generating low-shear-strength molybdenum-based lubricating films dominated by MoS₂ on worn surface, alongside iron-based compounds such as FeO and FeSO₄. Synergistic protection provided by physically adsorbed films and tribochemically generated reaction films collectively achieves outstanding stable friction-reducing and anti-wear performance. In contrast, at elevated temperatures of 125°C, intensified molecular thermal motion drastically weakens physical adsorption of DIOS base oil, inducing structural destabilization of adsorbed films. Meanwhile, thermal oxidation decomposition products of base oils occupy active metal surface adsorption sites and compete with MoDTC, hindering continuous formation of effective MoDTC adsorbed films. During friction processes, high-temperature environments preferentially promote oxidative decomposition of MoDTC, drastically increasing the proportion of Mo⁶⁺ species among decomposition products. This ultimately generates tribofilms mainly composed of MoO₃ and MoS_xO_y on worn surfaces. Such molybdenum oxides and oxyulfides lack intact layered structures

and possess high shear resistance, delivering far weaker friction-reducing effects than MoS₂. Although iron-based oxides and sulfides still form on contact surfaces, they cannot compensate for performance deficiencies of the molybdenum-based reaction films. Consequently, tribological systems exhibit aggravated COF fluctuations, enlarged wear scar diameter, and overall degraded lubrication efficiency at elevated temperatures.

Fig. 18 Schematic diagram of synergistic lubrication mechanism and temperature-dependent tribofilm formation of MoDTC in DIOS at 75°C and 125°C.

4 Conclusions

In this work, MoDTC was synthesized via a one-pot route using ammonium molybdate as the molybdenum raw material. Its tribological performance in base oils of different polarities under various loads and temperatures was systematically evaluated, and its lubrication mechanism in DIOS ester base oil was deeply explored. The main conclusions are summarized as follows:

1. In polar DIOS base oil, highly polar ester molecules preferentially adsorb onto metal surfaces to form dense physical adsorption layers, and MoDTC molecules further adsorb onto the outer side of ester films. The polar DIOS environment accelerates promotes MoDTC decomposition and promotes rapid amorphous tribofilm generation on metal surfaces, drastically shortening running-in periods. In contrast, MoDTC decomposition the PAO fully relies on localized high temperature induced by frictional shear, leading to slow tribofilm formation and prolonged running-in stages. In DIOS systems, MoDTC decomposition products deposit in ordered arrangements to form continuous, dense Mo/S-enriched composite tribofilms. In PAO6 systems, decomposition products tend to generate discontinuous tribofilms with poor substrate adhesion that readily detach under shear.
2. At 25 °C within the load range of 196–588 N, MoDTC additives improve the friction-reducing and anti-wear performance of DIOS base oil to varying degrees. The optimal enhancement effect is achieved under a medium load of 392 N, where the friction coefficient and wear scar diameter of the blend decrease by 50.0% and 23.3%, respectively, relative to neat DIOS. This result reveals excellent compatibility between MoDTC and DIOS ester oil under medium-load operating conditions.
3. MoDTC delivers outstanding friction-reducing and anti-wear performance at test temperatures of

25°C and 75°C. However, when temperature rises to 125°C, its friction-reducing capacity deteriorates significantly, evidenced by upward-trending, severely fluctuating friction curve. Nevertheless, MoDTC still maintains superior anti-wear effects compared with neat DIOS at 125 °C, yielding smaller wear scar diameters. XPS characterizations confirm distinct tribofilm component transitions with elevated temperature: dominant components shift from MoS₂ at low-to-moderate temperatures to MoO₃ and MoS_xO_y at 125 °C. Enrichment of these molybdenum oxide and oxysulfides is identified as the core factor driving COF increments at high temperatures. However, composite tribofilms can still form effective protective layers on metal surfaces to prevent severe adhesion and plastic deformation of mating metal substrates.

4. QCM-D adsorption tests further confirm that MoDTC exhibits stronger adsorption capacity and forms markedly thicker adsorbed films on metal surfaces at 75 °C relative to 125 °C. At 125 °C, thermal-oxidative decomposition products of DIOS base oil compete with MoDTC for active surface adsorption sites, hindering continuous formation of effective lubricating film. This competitive adsorption effect constitutes another key factor responsible for deteriorated MoDTC lubrication performance under high-temperature conditions.

Acknowledgments

The authors acknowledge financial support from National Key Research and Development Program of China (2023YFB3812104), Henan Province Science and Technology R&D Joint Fund (235101610007), Natural Science Foundation of Henan Provincial (262300421321, 262300421323), Postgraduate Education Reform and Quality Improvement Project of Henan Province (YJS2025GZZ28, YJS2024JD28), and Open Fund Project of National United Engineering Laboratory for Advanced Bearing Tribology (No. 202601, Henan University of Science and Technology).

Reference

- [1] Holmberg K, Kivikytö-Reponen P, Härkisaari P, Valtonen K, Erdemir A. Global energy consumption due to friction and wear in the mining industry. *Tribol Int* **115**: 116–139 (2017)
- [2] Holmberg K, Erdemir A. Influence of tribology on global energy consumption, costs and emissions. *Friction* **5**: 263–284 (2017)
- [3] Song J, Shi L, Ding H, Galas R, Omasta M, Wang W, Guo J, Liu Q, Hartl M. Effects of solid friction modifier on friction and rolling contact fatigue damage of wheel-rail surfaces. *Friction* **10**: 597–607 (2022)
- [4] Holmberg K, Erdemir A. The impact of tribology on energy use and CO₂ emission globally and

in combustion engine and electric cars. *Tribol Int* **135**: 389–396 (2019)

[5] Guegan J, Southby M, Spikes H. Friction modifier additives, synergies and antagonisms. *Tribol Lett* **67**: 83 (2015)

[6] Farfan-Cabrera L I, Hernández-Peña A, Resendiz-Calderon C D, Lee P, Sanchez C, Lee S, Erdemir A. Electrified four-ball testing of ZDDP and MoDTC as additives in low-viscosity synthetic oil. *Wear* **571**: 205835 (2025)

[7] Morina A, Neville A, Priest M, Green J H. ZDDP and MoDTC interactions and their effect on tribological performance – tribofilm characteristics and its evolution. *Tribol Lett* **24**: 243–256 (2006)

[8] Khaemba D N, Neville A, Morina A. A methodology for Raman characterisation of MoDTC tribofilms and its application in investigating the influence of surface chemistry on friction performance of MoDTC lubricants. *Tribol Lett* **59**: 38 (2015)

[9] Grossiord C, Varlot K, Martin J M, Le Mogne T, Esnouf C, Inoue K. MoS₂ single sheet lubrication by molybdenum dithiocarbamate. *Tribol Int* **31**: 737–743 (1998)

[10] Rai Y, Neville A, Morina A. Transient processes of MoS₂ tribofilm formation under boundary lubrication. *Lubr Sci* **28**: 449–471 (2016)

[11] Yamamoto Y, Gondo S, Kamakura T, Tanaka N. Frictional characteristics of molybdenum dithiophosphates. *Wear* **112**: 79–87 (1986)

[12] Peeters S, Charrin C, Duron I, Loehlés, Thiebaut B, Righi M C. Importance of the catalytic effect of the substrate in the functionality of lubricant additives: the case of molybdenum dithiocarbamates. *Mater Today Chem* **21**: 100487 (2021)

[13] Khaemba D N, Neville A, Morina A. New insights on the decomposition mechanism of Molybdenum dialkyldithiocarbamate (MoDTC): a Raman spectroscopic study. *RSC Adv* **6**: 38637–38646 (2016)

[14] Al Kharboutly M, Veryasov G, Gaval P, Verchere A, Camp C, Quadrelli E, Galipaud J, Reynard B, Cobian M, Le Mogne T, Minfray C. Mo (VI) dithiocarbamate with no pre-existing Mo–S–Mo core as an active lubricant additive. *Tribol Int* **154**: 106690 (2021)

[15] Trindade E D, Zuleta Durango A, Sinatora A. Friction and wear performance of MoDTC - containing and ester - containing lubricants over steel surfaces under reciprocating conditions. *Lubr Sci* **27**: 217–229 (2015)

[16] Komaba M, Kondo S, Suzuki A, Kurihara K, Mori S. The effect of temperature on lubrication property with MoDTC-containing lubricant —temperature dependence of friction coefficient and tribofilm structure—. *Tribol Online* **13**: 275–281 (2018)

[17] Garcia C E, Ueda M, Spikes H, Wong J S S. Temperature dependence of molybdenum dialkyl dithiocarbamate (MoDTC) tribofilms via time-resolved Raman spectroscopy. *Sci Rep* **11**: 3621 (2021)

[18] Fu X, Li Y, Su H, Cao L, Wan Y, Li R. Tribological interactions between TiN PVD coating and MoDTC under boundary lubrication conditions. *Vacuum* **195**: 110646 (2021)

[19] Balarini R, Diniz G A S, Profito F J, Souza R M. Comparison of unidirectional and reciprocating tribometers in tests with MoDTC-containing oils under boundary lubrication. *Tribol Int* **149**: 105686 (2020)

[20] Ruiz-Acero J, Kessler F, Costa H, Cousseau T. The effect of ethanol fuel dilution on oil performance and MoDTC tribofilms formation and composition. *Friction* **12**: 2108–2125 (2024)

[21] Kiw Y M, Adam P, Schaeffer P, Thiébaud B, Boyer C. Molecular evidence for sulfurization of molybdenum dithiocarbamates (MoDTC) by zinc dithiophosphates: a key process in their synergetic

interactions and the enhanced preservation of MoDTC in formulated lubricants?. *RSC Adv* **12**: 3542–3553 (2022)

[22] Wang W, Yu M, Ma J, Jia Y. Tribological properties of nanoparticles in the presence of MoDTC. *Lubricants* **11**: 132 (2023)

[23] Jia J, Lei X, Han K, Yue P, Fan S, Zhang C, Song N, Yang G, Zhang Y, Zhang S. Synergistic adsorption and lubrication mechanism of CeO₂ nanoparticle and MoDTC in lithium complex grease. *Tribol Int* **197**: 109819 (2024)

[24] Deshpande P, Minfray C, Dassenoy F, Le Mogne T, Jose D, Cobian M, Thiebaut B. Tribocatalytic behaviour of a TiO₂ atmospheric plasma spray (APS) coating in the presence of the friction modifier MoDTC: a parametric study. *RSC Adv* **8**: 15056–15068 (2018)

[25] Deshpande P, Dassenoy F, Minfray C, Jenei I Z, Le Mogne T, Thiebaut B. Effect of adding TiO₂ nanoparticles to a lubricant containing MoDTC on the tribological behavior of steel/steel contacts under boundary lubrication conditions. *Tribol Lett* **68**: 39 (2020)

[26] Fan Z, Wang S, Xiang Y, Liu Y, Yu Z, Ge X, Wang W. Synergetic lubrication between MoDTC and TiO₂ nano-additive: Dynamic evolution of tribofilm induced by tribocatalysis and tribomechanical effect. *Tribol Int* **207**: 110608 (2025)

[27] Peng F, Fan S, Song N, Gao C, Zhang S, Zhang Y. Effect of nickel acetyl acetate as lubricant additive in base oils with different molecular structure on in-situ formation and tribomechanism of carbon-based tribofilms of steel-steel sliding pair. *Tribol Lett* **72**: 56 (2024)

[28] Bian L, Song N, Yu L, Zhang Y, Zhang P, Zhang S. Susceptibility of Poly- α olefin and diisooctyl sebacate base oils with different polarities to oleic acid surface-capped ultra - small cerium oxide nanoparticle. *Lubr Sci* **36**: 478–488 (2024)

[29] Yao J, Fan S, Song N, Zhang Y, Zhang S. Surface regulation of silicon dioxide nanoparticle and its tribological properties as additive in base oils with different polarity. *Tribol Int* **191**: 109105 (2024)

[30] Naveira Suarez A, Grahn M, Pasaribu R, Larsson R. The influence of base oil polarity on the tribological performance of zinc dialkyl dithiophosphate additives. *Tribol Int* **43**: 2268–2278 (2010)

[31] Cen H, Morina A, Neville A. Effect of base oil polarity on the micropitting behaviour in rolling-sliding contacts. *Lubr Sci* **31**: 113–126 (2019)

[32] Jiang S, Martin J M, Adachi K, Murashima M. When ZDDPs meet polar base oils: A microscopic view on tribofilms growth. *Tribol Int* **220**: 111892 (2026)

[33] Han K, Fan S, Yang G, Zhang C, Zhang S, Zhang Y. Base oil polarity: A critical factor in the thermal stability of copper nanoparticles modified by dialkyl dithiophosphates. *Tribol Int* **211**: 110888 (2025)

[34] Barnes A L, Morina A, Andrew R E, Neville A. The effect of additive chemical structure on the tribofilms derived from varying molybdenum-sulfur chemistries. *Tribol Lett* **69**: 134 (2021)

[35] Sakurai T, Nishihara A, Handa T, Katoh H, Tomoda Y, Aoki K, Yoto M. Sulfur containing molybdenum dihydrocarbyldithiocarbamate compound. 1978.US4098705A.

[36] Tanaka N, Fukushima A, Tatsumi Y, Morita K, Saito Y. Process for producing molybdenum oxysulfide dithiocarbamate. 1997.US5631213A.

[37] Kamakura T, Tanaka N, Fukushima A, Tatsumi Y, Morita K. Powdery molybdenum oxysulfide dithiocarbamate composition, a process for producing same, and a grease composition containing the composition. 1996.US5494608.

[38] Chase K J, Tepper R J. Process for producing highly sulfurized molybdenum oxysulfide

dithiocarbamates. 2009.US7524799B2.

[39] McClain K S, Jolly K B, Ensor S J, Gershon D, Tynik R J, Vail C D, Wojtowicz S G. Process for preparing sulfurized molybdenum dialkylthiocarbamates. 2007.US2007249852A.

[40] Ye W, Gao C, Duan C, Ma Y, Zhang P, Duan H, Zhang S. Architecting cobblestone-like microstructures in PAI coatings: A dual-functional filler and lubricant polarity strategy for extreme wear resistance. *Colloid Surf A* **731**: 139082 (2026)

[41] Chen B, He T, Lu M, Zhao S, Xia Y, Yang Y, Song J, Zhang K. Ag/2D Ni-MOF nanohybrid as an efficient additive in castor oil: Synthesis, tribological performance, and lubrication mechanism. *Tribol Int* **225**: 112446 (2027)

[42] Hong Y, Mo Y, Lv J, Wang J. Tribological properties of polymer friction improvers combined with MoDTC/ZDDP at different temperatures. *Lubricants* **11**: 196 (2023)

[43] Homayoonfard M, Schroeder S L M, Dowding P, Delamore O, Morina A. Frictional behavior and tribofilm formation of organic friction modifiers under severe reciprocating conditions. *Langmuir* **41**: 29616–29626 (2025)

[44] Cyriac F, Yi T X, Poornachary S K, Chow P S. Effect of temperature on tribological performance of organic friction modifier and anti-wear additive: Insights from friction, surface (ToF-SIMS and EDX) and wear analysis. *Tribol Int* **157**: 106896 (2021)

[45] Liu K, Kang J, Zhang G, Lu Z, Yue W. Effect of temperature and mating pair on tribological properties of DLC and GLC coatings under high pressure lubricated by MoDTC and ZDDP. *Friction* **9**: 1390–1405 (2021)

[46] Wang L, Sun S, Zhang Y, Zhang C, Zhang S. Ionic liquid-functionalized ZnO nanomaterial: Multifunctional additives enhancing tribological performance and corrosion resistance in ester oil. *Tribol Int* **202**: 110320 (2025)

[47] Zhang D, Suo X, Wang J, Wang Y, Fan F, Wang L. The synergistic effect of novel anti-wear additive 1,3,4-thiadiazole mixed ammonium salt and MoDTC on tribological properties of FeCoCrNiMn alloy. *J Mater Res Technol* **38**: 5235–5249 (2025)

[48] Liu K, Qu Y, Zhang D, Liang B, Yan L. The potential of the synergistic use of SiO₂@silane-PEG with molybdenum dialkylthiocarbamate in water-based drilling fluid. *Colloid Surf A* **709**: 136101 (2025)

[49] Chen S, Fan S, Zhang C, Yang G, Yu L, Zhang S, Zhang Y. Synergistic lubrication of oleic diethanolamide - modified MoO₃ nanoparticles and water-based sulfur additives in steel-steel sliding systems under water-depleted conditions. *Lubri Sci* **38**: 23–35 (2026)

[50] Xu N, Wang C, Yang L, Jose G, Morina A. Probing the tribochemical impact on wear rate dynamics of hydrogenated amorphous carbon via Raman-based profilometry. *ACS Appl Mater Inter* **14**: 2071–2081 (2021)

Author Biography



Yunhan Zhang received her bachelor degree in Materials Science and Engineering from Henan University Minsheng College in 2023. She was a postgraduate student at the Institute of Nanoscience and Engineering, Henan University, Kaifeng, China. She obtained her Master's degree in Chemistry in 2026. Her main research interests focus on the development of high-performance sulfur-containing lubricant additives and their tribological applications.



Guangbin Yang received his Ph.D. in Condensed Matter Physics from Henan University in 2011. He is currently a professor at the Institute of Nanoscience and Engineering, Henan University. His research focus on material tribology and interfacial lubrication. He has published more than 90 papers in authoritative domestic and international journals, presided over and participated in a number of national and provincial-ministerial research projects. He has been awarded three provincial-ministerial-level science and technology awards and holds more than 10 authorized national invention patents.



Shengmao Zhang received his Ph.D. degree in physical chemistry from the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China, in 2005. Now, he is a professor at Henan University, China. His current research interests include nanoparticle lubricant additives, high-performance lubricants and functional materials, and tribology of materials.