DOCTORAL THESIS

Green-lubricated contacts through in-situ tribofilm formation using environmentally adapted nanotechnologies

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Machine Elements

Luleå University of Technology

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Abstract

Growing environmental regulations that limit sulfur and phosphorus in engine lubricants have created an urgent need to reduce or replace zinc dialkyldithiophosphate, commonly used anti wear additive, without compromising tribological performance. This thesis tackles that challenge head on. It develops and explains, at a mechanistic level, a new multi additive lubricant formulation that combines glycerol monooleate, carboxylated nanodiamonds, and two families of two dimensional MXenes, namely $Mo_2TiC_2T_x$ and $Ti_3C_2T_x$, dispersed in a polyalphaolefin base oil. The central hypothesis is that well-designed interactions between these additives can promote the formation of durable, low-shear tribofilms under boundary lubrication conditions that can match or even surpass the protection traditionally provided by ZDDP-based formulations.

The research is structured into four experimental phases, each building toward lubricant systems with progressively lower sulfur and phosphorus content. In the first phase, blending nanodiamonds, glycerol monooleate, and a small amount of ZDDP in the base oil led to marked reductions in both friction and wear compared with conventional formulations. A key outcome was the discovery of tribochemical interactions between carboxylated nanodiamonds and glycerol monooleate at around 80 °C, which significantly accelerated tribofilm formation. The observed reduction in friction was linked to nanodiamonds becoming embedded within a glycerol monooleate derived tribofilm, along with rolling effects, mechanical interlocking, and micro scale surface polishing. The second phase explored how nanodiamonds perform in combination with molybdenum dithiocarbamate. The results showed that optimal tribological behaviour occurs when nanodiamonds are fully incorporated within MoDTC derived tribofilms containing MoS_2. Performance was found to depend strongly on the surrounding additive package, highlighting that synergistic formulation design is not accidental but essential for reliable and repeatable performance. In the third phase, attention shifted to the use of $Mo_2TiC_2T_x$ MXene together with glycerol monooleate and reduced ZDDP content. Although dispersion proved challenging, these formulations formed multilayered tribofilms enriched with MXene, leading to substantial reductions in friction and wear compared with the base oil alone. These results demonstrate a technically viable route to lowering sulfur and phosphorus while maintaining effective anti-wear performance in realistic lubricant systems. The fourth and final phase investigated a formulation that was almost free of ZDDP, consisting of $Ti_3C_2T_x$ MXene, nanodiamonds, and glycerol monooleate. This system produced uniform and continuous tribofilms with an average thickness of about 150 nanometres, exhibited excellent wear resistance under high contact pressure.

Overall, this work provides the first systematic examination of multi additive synergy involving glycerol monooleate, nanodiamonds, and MXenes under boundary lubrication conditions. It delivers nanoscale insight into how interactions between additives influence tribofilm composition, thickness, and shear behaviour. The findings show that newly developed additive formulation reduced or eliminated ZDDP and in some cases outperform, conventional anti wear benchmarks. Importantly, the thesis lays out a clear

and evidence-based pathway toward next-generation lubricants that balance environmental requirements with high tribological performance, with clear relevance to automotive, aerospace, and industrial applications.

Appended papers

Paper 1: Piya, A.K., Yang, L., Omar, A.A.S., Emami, N. and Morina, A. 2024. Synergistic lubrication mechanism of nanodiamonds with organic friction modifier. *Carbon (New York)*. 218.

Paper 2: Piya, A.K., Yang, L., Emami, N. and Morina, A. 2025. Effect of Nanodiamonds on Friction Reduction Performance in Presence of Organic and Inorganic Friction Modifiers. *Lubricants*. **13**(1), p.1.

Paper 3: Piya, A.K., A. Al Sheikh Omar, Yang, L., Emami, N. and Morina, A. Application of $Mo_2TiC_2T_x$ MXenes Based Lubricant Additives for the Development of Low Concentration S and P Lubricants.

Paper 4: Piya, A.K., Ajay Pratap Singh Lodhi, Yang, L., Emami, N. and Morina, A. Tribological Performance of $Ti_3C_2T_x$ MXenes as Lubricant Additives: Interactions with Nanodiamonds and Organic Friction Modifier.

Conference contribution

Afrina Khan Piya, Liuquan Yang, Ardian Morina, Nazanin Emami, *Friction Reduction Performance of Nanodiamonds in Presence of Organic Friction Modifier*, 77th Annual Meeting & Exhibition, STLE 2023, Oral presentation.

Afrina Khan Piya, Liuquan Yang, Nazanin Emami, Ardian Morina, *Improved Tribological Performance of Nanodiamonds in Presence of Organic Friction Modifier*, 9th International Tribology Conference, ITC Fukuoka 2023, Oral presentation.

Afrina Khan Piya, Liuquan Yang, Nazanin Emami and Ardian Morina, *Effect of $Ti_3C_2T_x$ MXene as lubricant additive on friction reduction performance*, 48th Leeds-Lyon Symposium on Tribology, Leeds, UK, 2023, Oral presentation.

Afrina Khan Piya, Liuquan Yang, Nazanin Emami and Ardian Morina, *Tribological Performance Evaluation of $Ti_3C_2T_x$ MXene as Lubricant Additive in Presence of Organic Friction Modifier*, 49th Leeds-Lyon Symposium on Tribology, Leeds, UK, 2024, Oral presentation.

Afrina Khan Piya, Liuquan Yang, Nazanin Emami and Ardian Morina, *Frictional performance of $Ti_3C_2T_x$ MXenes with nanodiamonds in presence of Organic Friction Modifier*, Ecotrib 25, 9th European Conference on Tribology, 2025, Oral presentation.

Abbreviations

2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic Force Microscopy
Ag	Silver
Al	Aluminium
Al_2O_3	Aluminium oxide
ASTM	American Society for Testing and Materials
Bi	Bismuth
Co	Cobalt
COF	Coefficient of Friction
CNT	Carbon Nanotubes
Cu	Copper
CuS	Copper Sulfide
DA	Dioctylamine
Fe	Iron
FeS	Iron Sulfide
FIB	Focused Ion Beam
FMs	Friction Modifiers
GMO	Glycerol Monooleate
GO	Graphene Oxide
h-BN	Hexagonal Boron Nitride
HRTEM	High-Resolution Transmission Electron Microscopy

MoDTC	Molybdenum Dithiocarbamate
MoS_2	Molybdenum Disulfide
MWNTs	Multi-Walled Carbon Nanotubes
ND	Nanodiamond
NPs	Nanoparticles
OA	Oleic Acid
OFMs	Organic Friction Modifiers
PAO	Polyalphaolefin
PGZ	PAO + GMO + ZDDP
PN0.05	PAO + Nanodiamonds 0.05 wt%
PGZN0.05	PAO + GMO + ZDDP + Nanodiamonds 0.05 wt%
PMoGZN	PAO + MoDTC + GMO + ZDDP + Nanodiamonds
PGMox	PAO + GMO + $Mo_2TiC_2T_x$
PZMox	PAO + ZDDP + $Mo_2TiC_2T_x$
PGZMox	PAO + GMO + ZDDP + $Mo_2TiC_2T_x$
Pd	Palladium
Pt	Platinum
SEM	Scanning Electron Microscope
SIMS	Static Secondary Ion Mass Spectrometry
SiO_2	Silicon Dioxide
SWCNTs	Single-Walled Carbon Nanotubes
TA	Trihexylamine
TMDs	Transition Metal Dichalcogenides
WS_2	Tungsten Disulfide

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PART A: COMPREHENSIVE SUMMARY

1 Chapter 1: Introduction

1.1 Background

CO_2 emissions, climate change, and energy consumption remains critical global challenges that require immediate, sustainable solutions. High energy demand contributes significantly to pollution in various forms, resulting in elevated CO_2 emissions [1]. A substantial proportion of energy is consumed in overcoming friction and wear in various mechanical systems, particularly within industrial, power generation, and transportation sectors. Recent studies indicate that approximately 119 EJ of global energy consumption, around 23% of the total energy is associated with tribological contacts [1,2]. Of this, nearly 13% (16 EJ) is expended on remanufacturing components damaged by wear-related failures, while the remaining 87% (103 EJ) is consumed in overcoming friction. Consequently, friction and wear collectively account for approximately 8,129 Mt of annual CO_2 emissions [3]. UK government statistics further highlight the growing energy demand in transportation. In 2023 and 2024, energy consumption in this sector increased by approximately 2.9%, reaching 54.0 Mt. In 2024, transportation represented about 42% of global energy use, with road transport contributing 71.7%, aviation 25%, rail 1.8%, and marine 1.5% as shown in Figure 1-1 [4]. These underscore the urgent need for advanced tribological solutions to reduce frictional losses and wear, thereby improving energy efficiency and mitigating environmental impact.

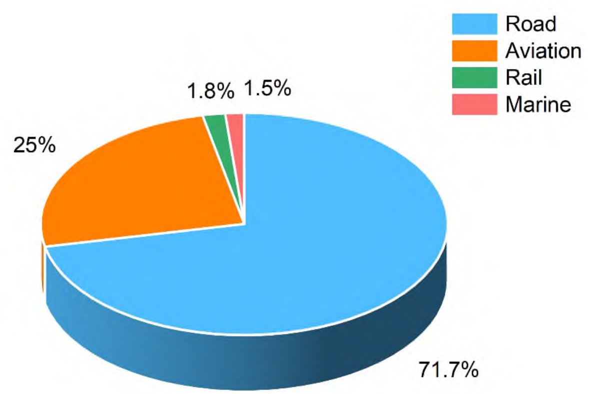

Figure 1-1Global energy consumption by transportation vehicles [4].

To address these challenges, the most effective approach to minimizing friction and wear is through the use of solid, gaseous, or liquid lubricants [5]. The principal role of lubricants is to protect components and tools from wear, maintain surface integrity, and ensure smooth operation thereby extending service life. Among the different types, liquid lubricants offer distinct advantages, including corrosion prevention, mechanical noise reduction, heat dissipation, removal of wear debris, and function as a liquid seal [6]. These properties are essential for safeguarding machine elements under heavy loads while reducing energy consumption [7]. Modern lubricants are formulated to interact with materials and surface coatings to reduce friction and wear. Fully formulated oils typically consist of a base oil, often supplemented with synthetic and chemical additives that enhance specific tribological properties [8]. Among these additives, anti-wear agents and friction modifiers play a critical role in protecting surfaces and reducing friction under boundary and mixed lubrication regimes [9,10]. Zinc dialkyldithiophosphate (ZDDP) remains the most extensively used anti-wear additive; it decomposes under heat and pressure to form a phosphate-rich tribofilm via tribochemical reactions, which acts as a protective barrier on contacting surfaces [11]. Similarly, molybdenum dithiocarbamate (MoDTC) is the most commonly used friction modifier, valued for its ability to form low-shear MoS_2 tribofilm at the interface [12]. Despite their superior tribological performance, these additives contain elements such as phosphorus, zinc, and sulfur, which pose environmental concerns, particularly in engine applications [13]. Due to the use of these toxic elements, stringent environmental regulations have been employed to lessen their impact. This has given rise to the promising field of green tribology, which involves reducing natural petroleum usage, utilizing natural materials, increasing energy efficiency by reducing pollution and emissions, improving equipment performance, and shortening the maintenance cycle for sustainable and environmentally friendly designs. As a result, the automobile industry has shifted their focus towards using low-SAPS (sulphated ash, phosphorus, sulfur) engine oils. To achieve the goal, introducing new technologies, chemical additives and complete integration of more environmentally friendly lubricant technology is necessary [14] .

To comply with increasingly stringent environmental legislation, alternative solutions are being actively pursued to replace conventional lubricant additives such as ZDDP and MoDTC. Despite extensive research efforts, the challenge of developing phosphorus-free substitutes that maintain or exceed the tribological performance of these established additives remains unresolved. This difficulty arises from the unique multifunctional roles that ZDDP and MoDTC fulfil in boundary lubrication regimes, including anti-wear protection and friction reduction through tribochemical film formation. Consequently, the current research focus has shifted towards exploring individual additives and formulating synergistic combinations that can deliver comparable or superior tribological behaviour while meeting environmental compliance requirements.

The subsequent subsections provide an in-depth examination of friction modifiers as lubricant additives, highlighting their relevance in modern lubrication strategies. Particular emphasis is placed on organic friction modifiers and nanoparticle-based systems, which have emerged as promising candidates for next-generation formulations. The discussion includes an analysis of how the intrinsic properties of nanoparticles such as chemical composition, particle size, and morphology, affect their tribological performance under varying operating conditions. Furthermore, recent advancements in nanoparticle additives, specifically nanodiamonds and MXenes, are reviewed in detail. Their lubrication mechanisms, interaction with base oils and other additives, and potential for integration into environmentally compliant lubricant systems are critically assessed to establish their viability as alternatives to traditional additives.

1.2 Research Gap

Despite extensive studies and substantial progress in nanoparticles, friction modifiers and other widely used additives in the lubrication industry, anti-wear additives, such as ZDDP, and friction modifier additives, like MoDTC, remain the widely used solutions for protecting the surfaces and reducing friction in boundary lubricated contacts in engines. However, the presence of P and S in these additives remains an unsolved concern, as these elements are shown to contaminate exhaust gas aftertreatment systems, causing severe environmental impacts from engines. A comprehensive review of the literature reveals that, despite significant advancements, the industry remains constrained by a narrow focus on single-additive replacements for ZDDP or MoDTC. This strategy has consistently failed to deliver formulations capable of meeting both friction and anti-wear demand under boundary lubrication in real-world operating conditions. This thesis identifies several critical gaps and proposes future research directions:

1. Insufficient understanding of multi-additive synergy: The co-assembly and functional role of GMO, nanodiamond, and MXene in forming durable, low shear tribofilm is not systematically characterised.
2. Clear mechanism of friction and wear reduction: Currently, there is no universal rule or model that explains how additive formulations achieve friction and wear reduction. The mechanisms remain poorly defined, making it difficult to predict performance or design effective combinations.
3. Tribochemical behaviour of MXene: Although MXene have shown strong potential as solid lubricants and coatings, their behaviour in oil-based systems remains poorly understood. Key aspects such as elemental partitioning (e.g., Mo enrichment within tribolayers versus Ti retention at deeper interfaces) and interactions with OFM-derived surface species are not yet clarified at the nanometre scale or across the critical timeframes from run-in to steady-state under boundary lubrication conditions.
4. Benchmarking against regulatory endpoints: Current research lacks direct, head-to-head comparisons between ZDDP-reduced or ZDDP-free multi-additive formulations under identical boundary lubrication conditions. Comprehensive evaluations, including friction and wear measurements alongside advanced surface analytics are scarce, creating a critical gap that prevents evidence-based pathways for regulatory-compliant additive substitution.

1.3 Research Questions

This thesis addresses the following research questions and based on these the objectives are developed:

RQ1: How do nanodiamond (ND) and glycerol monooleate (GMO) additives, applied individually and in combination, influence friction coefficient, wear rate, and tribofilm formation under boundary lubrication conditions, and how do their underlying mechanisms compare to those of ZDDP?

RQ2: What are the tribological and tribochemical effects of combining NDs, GMO, MoDTC, and ZDDP in multi-additive formulations, and do these combinations produce synergistic or antagonistic interactions with respect to friction, wear rate, and tribofilm chemistry?

RQ3: How does $Mo_2TiC_2T_x$ MXene influence friction and wear performance when used as a lubricant additive individually and in combination with GMO and ZDDP under boundary lubrication, and can it achieve tribological performance comparable to or exceeding that of ZDDP relative to a base-oil reference?

RQ4: What tribological performance can a ZDDP-free ternary formulation of NDs, GMO, and $Ti_3C_2T_x$ MXenes achieve under boundary lubrication, and what are the composition, structure, and mechanistic basis of the resulting tribofilm relative to conventional ZDDP/MoDTC-based formulations?

1.4 Outline of Thesis

This thesis is organised as follows:

- Chapter 1 provides the background, statement of the research problem, identification of research gaps, aims and objectives, and outline of the thesis followed by a comprehensive review of the state of the art in relevant fields, covering boundary lubrication mechanisms, conventional lubricant additives, organic friction modifiers, nanoparticle-based additives, and two-dimensional MXene nanomaterials.
- Chapter 2 presents the materials, experimental methods, and characterisation techniques employed throughout the research, including tribological testing procedures, surface analysis methods, and the justification of experimental design decisions.
- Chapter 3 provides a comprehensive cross-phase discussion of the principal findings, comparing tribological performance and tribofilm characteristics across all four phases and synthesising the mechanistic understanding developed throughout the research.
- Chapter 4 outlines the limitations of the present study and identifies directions for future research followed by the summary and conclusions of the thesis, highlighting the key contributions to knowledge.

Appended papers:

- Paper 1 reports the investigation of synergistic interactions between nanodiamonds, GMO, and low-concentration ZDDP, addressing Objective 1 and RQ1.
- Paper 2 presents the investigation of nanodiamonds in combination with GMO, MoDTC, nanodiamonds and low-concentration ZDDP, addressing Objective 2 and RQ2.
- Paper 3 reports the evaluation of $Mo_2TiC_2T_x$ MXene as a lubricant additive in combination with GMO and low-concentration ZDDP, addressing Objective 3 and RQ3.
- Paper 4 presents the investigation of $Ti_3C_2T_x$ MXene combined with nanodiamonds and GMO in a fully phosphorus- and sulfur-free formulation, addressing Objective 4 and RQ4.

1.5 Literature Review

1.5.1 Role of Friction Modifiers (FMs) in Friction Reduction

A significant amount of research is dedicated to identifying the most effective strategies for reducing friction and associated energy consumption in various mechanical systems. Among these strategies, lubrication remains one of the most efficient approaches for reducing friction in tribological contacts. Over recent decades, liquid-based lubricants have been broadly employed across industrial applications to optimise the coefficient of friction (COF) and dissipate excess heat generated during mechanical operation. Lubrication regimes are in general classified into four categories: (a) hydrodynamic lubrication, (b) elastohydrodynamic lubrication, (c) mixed lubrication, and (d) boundary lubrication. Of these, friction and wear are most pronounced in the boundary and mixed lubrication regimes. These lead to increased wear rates and significant energy losses in machine components. Under conditions of low speed and high load, typical of compressors, pumps, bearings, gears, and valve trains, the boundary lubrication regime predominates. In this regime, the average lubricant film thickness falls below the roughness scale, resulting in partial metal to metal contact where asperities bear a substantial portion of the load. This condition promotes complex interfacial phenomena, including fracture, abrasion, adhesion, wear, and tribochemical reactions [15] .

Under such circumstances, liquid lubricants alone are insufficient to prevent direct surface contact and associated wear. To address this limitation, two complementary approaches have been developed: (i) the incorporation of friction modifier additives into lubricants to reduce friction and enhance surface lubricity, and (ii) the optimisation of lubricant rheology to minimise agitation, hydrodynamic shear, and pumping losses. When applied concurrently, friction modifiers exhibit maximum effectiveness as lubricant viscosity decreases, and thin hydrodynamic films separate the contacting surfaces.

With the growing need to lower greenhouse gas emissions and improve fuel economy, friction modifiers have attracted considerable attention for integration into lubricant formulations. These additives can be primarily classified into four foremost categories [16]:

- Organic friction modifiers (OFMs): Typically, amphiphilic surfactants, widely applied in modern fuels and engine oils.
- Organo-molybdenum compounds: Oil-soluble additives, offer friction-reducing and anti-wear properties, originally developed for gear oils.
- Functionalised polymers: Designed for polar tribological surfaces to enhance film formation and reduce friction.
- Nanoparticles: Emerging as a promising class of friction modifiers due to their unique size-dependent properties.

Studies have demonstrated that friction modifiers reduce friction through various mechanisms, including Van der Waals adsorption, formation of high-viscosity interfacial layers, and nano-rolling effects [17]. These mechanisms collectively contribute to improved tribological performance under boundary lubrication conditions.

1.5.2 Organic Friction Modifiers (OFMs)

The concept of reducing friction by adding fatty acids to mineral oils was first introduced in 1915. This discovery marked the beginning of extensive research into the fundamental mechanisms of organic friction modifiers (OFMs). Irving Langmuir is widely regarded as one of the pioneers in this field; in 1920, he described the “floating” phenomenon, which proposed that bonding interactions between active functional groups, such as carboxyl groups and double bonds and the surface could enable the formation of a monomolecular layer of long-chain fatty acids. This adsorbed layer created a low-shear interface and significantly reduced the coefficient of friction [18].

Organic friction modifiers possess an amphiphilic molecular structure comprising a non-polar hydrocarbon tail and a polar head group (Figure 1-2). The polar head group strongly adsorbs onto polar metallic or ceramic surfaces. At the same time, the hydrocarbon tail extends into the lubricating oil, forming a low-shear hydrocarbon interface against an opposing surface. Common OFMs, for example, amines, fatty acids, amides, and esters, typically bind to surfaces through Van der Waals forces between lateral side chains and hydrogen bonding between polar end groups and hydroxyl groups on the metal surface [16]. Consequently, OFMs generally form thin, weakly bound boundary films that are susceptible to displacement at elevated temperatures or by competing additives within the lubricant formulation. Structurally, OFMs are characterised by non-polar, linear hydrocarbon chains terminated by a polar functional group responsible for surface adhesion [19].

For effective friction reduction, OFMs must form moderately dense monolayers that facilitate lateral Van der Waals interactions between adjacent hydrocarbon chains, ideally oriented vertically to maximise packing density [20]. These adsorbed layers exhibit friction-reducing properties; however, their characteristics may evolve during sliding contact. Rubbing can promote multilayer formation or induce tribochemical reactions, altering the film's structure and performance [21]. The friction reducing capability of OFMs is strongly influenced by the terminal functional group and the length of the hydrocarbon chain [22,23]. Figure 1-2 illustrates different structures of the OFM additives: (a) oleic acid, (b) glycerol monooleate (GMO), (c) oleylamine (OA), (d) dimethylhexadecylamine (DM16), (e) dioctylamine (DA), (f) trihexylamine (TA) and (g) glycerol [24].

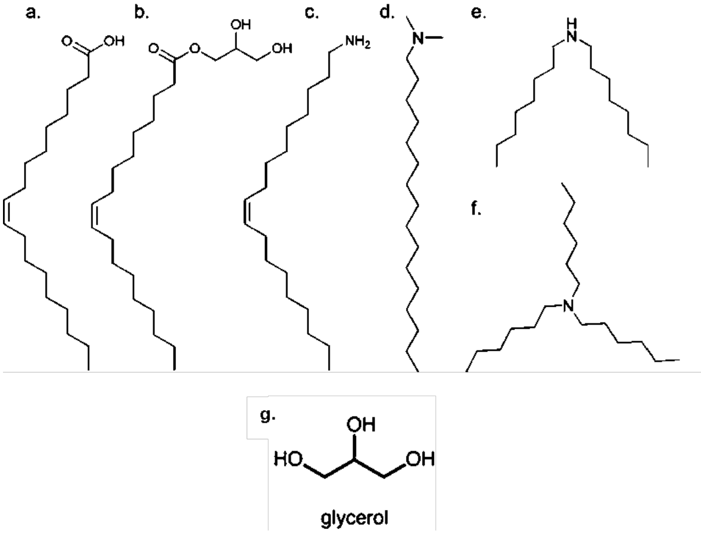

Figure 1-2 Structures of the OFM additives, (a) oleic acid, (b) glycerol monooleate (GMO), (c) oleylamine (OA), (d) dimethylhexadecylamine (DM16), (e) dioctylamine (DA), (f) trihexylamine (TA),(g) glycerol [24].

Researchers have projected a thick-film action model in which friction modifiers form viscous layers on metallic surfaces with thicknesses ranging from several nanometers to hundreds of nanometers [25]. Although the precise scientific conditions required for the formation of monolayers or thick films by organic friction modifiers remain unclear, studies have demonstrated that thick films can develop when long-chain carboxylic acids react chemically with the surface to produce metal carboxylates [26].

The growing emphasis on *green lubrication* or environmentally friendly lubrication has led to increased interest in vegetable oils that are biodegradable and their end products as alternatives to conventional lubricants that are petroleum-based and additives. Minami et al. observed that the traditional fatty acids exhibit insufficient adsorption activity when they are dissolved in polar synthetic oils, for instance, polyether. To enhance their friction-reducing capability, an additional carboxyl group was introduced, adjacent to the original group, thereby increasing molecular polarity and improving their effectiveness as friction modifiers [27].

Fatty acids were the earliest form of organic friction modifiers (OFMs); however, they were later found to cause severe corrosion of certain bearing metals, including cadmium, lead, tin, and copper. Consequently, slowly replaced by less corrosive amphiphilic compounds, for instance, esters, amines, and amides [28]. Among these, glyceryl monooleate (GMO), is widely used commercially as a lubricant and fuel additive. According to the Bowden–Tabor model, GMO has a well-known lubrication mechanism in steel/steel contacts: GMO undergoes hydrolysis to release straight-chain carboxylic acids, which act as friction modifiers [29]. In contrast, when interacting with diamond-like carbon (DLC) coatings, GMO functions primarily as an ester rather than a carboxylic acid, with hydroxyl groups playing a critical role in the adsorption process [30].

Experimental studies have shown that under rubbing conditions, GMO hydrolyses in the presence of trace amounts of water to produce carboxylic acid molecules, which subsequently adsorb onto metal surfaces [31]. These chemical interactions can be synergistic or antagonistic, depending on various aspects such as the concentration and chemical composition of the additives. For example, OFMs and zinc dialkyldithiophosphate (ZDDP) have demonstrated both synergistic and antagonistic effects under different conditions [32]. Similarly, competitive surface adsorption has been found between OFMs and extreme pressure (EP) additives, which are sulfur-based, resulting in antagonistic behavior [33]. In some instances, mixing over based calcium sulphonate detergents with GMO has also produced antagonistic effects, reducing component lifetime. Further studies have investigated the performance of OFMs in complex lubricant formulations. For instance, in continuously variable transmission (CVT) lubricants, OFM, as oleic acid, offered negligible reduction in friction and, in some cases, from the surface, detergents were displaced by it. Nonetheless, GMO improved friction reduction properties, although wear protection was not improved [34]. Research involving multiple friction modifiers revealed that combinations such as GMO and oleyl amide exhibited no synergistic effect, while mixtures of GMO with polymeric friction modifiers demonstrated positive interactions [35]. Cyriac et al. [9] have shown an improved frictional performance for lubricants containing mineral oil, ZDDP and GMO. Another study showed that a combination of MoDTC, GMO, and ZDDP produced a synergistic effect, reducing friction by approximately 30–50% when blended with PAO oil and palm trimethylolpropane ester [36]. Based on the above review, GMO was selected as organic friction modifier for this experimental work.

1.5.3 Nanoparticles as Friction Modifiers

In recent years, nanoparticles as lubricant additives have drawn significant attention owing to their ability to reduce friction and wear effectively. Their nanoscale dimensions (<100 nm) enable them to penetrate contact regions, while their superior thermal stability compared to organic additives and the diversity of available chemistries make them highly suitable for tribological applications. Furthermore, the exceptional lubricating properties of nanoparticle-based additives position them as promising alternatives to conventional additives currently employed in lubricants. These nanoparticles have demonstrated potential to enhance engine performance, improve fuel efficiency, optimise combustion behavior, reduce exhaust emissions, and minimise evaporation losses under various operating conditions [37]. The chemical composition of nanoparticles plays a critical role in determining their interaction with lubricants and contacting surfaces, as their physical and chemical characteristics vary significantly across different material classes. A broad spectrum of nanoparticles has been investigated for use in lubrication systems. Nanoparticles can be categorised into different groups based on their elemental composition: carbon and its derivatives, rare-earth compounds, metals, metal oxides, sulfides, nanocomposites, and others [38]. Additionally, clays have been identified as a separate category because of their tribological properties and exceptional layered structure [39]. A summary of the major classes of nanoparticles employed as lubricant additives is presented below.

Table 1-1 Summary of nanoparticles as lubricant additives [40].

Types	Nanoparticles
Carbon and its derivatives	Graphene, Graphene Oxide, Nanodiamond, Single-Walled Carbon Nanotubes (SWCNT), Multi-Walled Carbon Nanotubes (MWNTs)
Metals	Sn, Fe, Bi, Cu, Ag, Ti, Ni, Co, Pd, Au
Metal Oxides	ZrO_2, TiO_2, Fe_3O_4, Al_2O_3, ZnO, CuO
Metal Sulfides	CuS, WS_2, MoS_2, $NiMoO_2S_2$
Rare earth compounds	LaF_3, CeO_2, Y_2O_3, $CeBO_3$
Clays	Montmorillonite, Halloysite, Kaolinite
Nanocomposites	Cu/SiO_2, Cu/Graphene Oxide, Al_2O_3/SiO_2, Serpentine/La$(OH)_3$, Al_2O_3/TiO_2,
Borates	$Ca_3(BO_3)_2$
Boron Based	h-BN
Others	SiO_2, PTFE, $CaCO_3$, $ZnAl_2O_4$, Zeolite, MXenes Hydroxide, Serpentine

1.5.3.1 Metals Nanoparticles

Over the past decade, metallic nanoparticles (NPs) have been significantly investigated for their exceptional chemical and physical properties, making them highly suitable as friction modifiers (FMs) in lubricating systems. These nanoparticles exhibit advantageous characteristics such as low melting points, high surface area, and low shear stress. Their excellent anti-wear and friction-reducing abilities, combined with a self-repairing function, have positioned them as promising additives for advanced lubrication technologies. Common metallic nanoparticles include copper (Cu), bismuth (Bi), palladium (Pd), cobalt (Co), zinc (Zn), tin (Sn), iron (Fe), nickel (Ni), aluminium

(Al), and silver (Ag), among others [41]. Metallic nanoparticles offer several key benefits in tribological applications:

1. **Formation of compliant layers:** When physically pressed into the contact zone, nanoparticles can create a nanoparticle-containing layer that reduces shear resistance and asperity contact pressure, thereby lowering friction.
2. **Tribofilm development:** Nanoparticles can contribute to the development of tribofilm on the contacting surface, which act as protective layers and reduce friction.
3. **Rolling effect:** Nanoparticles can roll between frictional surfaces, functioning as nano-bearings and further decreasing friction.
4. **Sintering phenomenon:** Under operational conditions involving high pressure and temperature, nanoparticles may undergo sintering, which can enhance surface protection and repair.

These mechanisms collectively enable metallic nanoparticles to improve lubrication performance under severe operating conditions, making them an attractive alternative to conventional friction modifiers [38].

A detailed literature review of tribological properties of different metal nanoparticles is comprised in next table.

Table 1-2 Metal nanoparticles with the testing conditions and results

Nanolubricant details						Test Parameter				Results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Tem. and duration	Wear and Friction Reduction	Optimum Conc.	Ref.
Cu	SAE grade 15W-40	2.5, 5,7.5 and 10 wt%	50 nm	Mechanical agitation & Ultrasonic dispersion	30 min	Ball-on-disk	50 N	10-30 Hz	Room temp., 30 min	synergistic effect on friction and wear,COF ~0.10–0.11 and wear volume ~4 × 10^{-3} mm^3	7.5 wt%	[42]
	Polyalphaolfin (PAO6)	0.5, 2 wt%	25 nm	Ultrasonic probe	30 min	Four ball, Block and ring	165N, medium load condition	1 m/s, 1470 rpm	Room temp., 3066 m total distance	With wear reduced 31–50% at 0.5 wt%, Not reported as single COF value	0.5 wt%	[43]
Fe, Cu, Co	SAE 10 mineral oil	0.5 wt%	50–80 nm	Converse emulsion water-in-lubricant solution (CEWLS)		Four ball tester	150 N	1420 rpm	1 hr	A reduction of wear loss 11% (Co),23% (Fe), 47% (Cu) and friction reduction up to 20% (Co), 39% (Fe), 49% (Cu) COF Cu: ~0.03–0.04 equiv.; Fe: ~0.04–0.05; Co: ~0.05 (from friction torque data) Wear: WSD: Cu ~0.33 mm; Fe ~0.47 mm; Co ~0.57 mm vs SAE 10 ~0.63 mm	0.5 wt%	[44]
Al	Paraffin Oil	0.025–5 wt%	65 nm	Ultrasonic stirring	30 min	Ball-on-ring tester	50–300 N	500 rpm	Room temp., 1 h	Improved friction and wear	0.5 wt%	[45]

Nanolubricant details						Test Parameter				Results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Tem. and duration	Wear and Friction Reduction	Optimum Conc.	Ref.
										COF~0.07–0.08 (at 0.5 wt%, stable) vs pure paraffin ~0.12 Wear: WSD at 0.5 wt%, 2.25 GPa: ~0.75 mm vs pure paraffin ~1.20 mm		
Ni	Polyalphaolfin (PAO6)	0.05 wt%	7.5–13.5 nm,28.5nm	In situ one-step thermal decomposition; oleylamine + oleic acid surface capping	Room temp., 30 min	Four-ball tester	300 N	1,450 rpm	30 min	Reduction in wear loss to 0.47–0.54 and friction reduction to 0.78–0.68	0.05 wt%	[46]

Despite their significant tribological properties, metal nanoparticles face several challenges that limit their use as lubricant additives. One of the main issues is their tendency to agglomerate and settle over time, which reduces the amount of active material available at the sliding interface and gradually weakens lubrication performance. In addition, metal nanoparticles such as copper and iron can oxidise under the high temperatures and pressures typical of engine operation, forming hard oxide particles that behave abrasively and can accelerate wear instead of preventing it. There are also important environmental and health concerns linked to the release of metallic nanoparticles, particularly in engine applications where lubricant degradation, leakage, or disposal is necessary [38].

1.5.3.2 Metal Oxide Nanoparticles

Metal oxide nanoparticles, for example TiO_2, CuO, Fe_3O_4, ZnO, and Al_2O_3 have been widely studied as lubricant additives due to their promising tribological properties. These nanoparticles exhibit lubrication mechanisms similar to metallic nanomaterials, involving the rolling effect, sintering or self-repairing behavior, and, most importantly, the formation of tribofilm or adsorption layers that reduce friction. Luo et al. researched about the Al_2O_3 nanoparticles and their tribological performance using two types of tribometer in pure lubricating oil. Their findings revealed a decrease in the coefficient of friction (COF) value by 17.61%, attributed to the formation of a protective film on the contact surface and the rolling mechanism [47]. However, the addition of Al_2O_3 to PAO and SAE 75W-85 oils resulted in detrimental effects on tribological performance [48]. Similarly, CuO and TiO_2 nanoparticles have been employed as lubricant additives, with experimental studies demonstrating friction reduction through the rolling effect at elevated temperatures, as well as viscosity-related improvements at lower temperatures [49,50].

Magnetic Fe_3O_4 NPs dispersed in lubricating oil with an average particle diameter of 11.7 nm showed COF reduction by 45% and wear scar diameter reduction by 30%. They suggested that the rolling mechanism for the improved tribological [51]. More studies on metallic oxides are shown in the Table 1-3.

Table 1-3 Metal oxide nanoparticles with the testing conditions and results

Nanolubricant details						Test Parameter				Results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Temp. and duration	Wear and Friction Reduction	Optimum Conc.	Ref.
Al_2O_3	SAE20W40	0–1 wt%	40–80 nm	Magnetic stirrer	at 1000 rpm for 20 hrs	Pin-on-disc	160 N	1,200 rpm		Minimum COF = 0.011 at 0.8 wt%, 60 nm, 160 N, 1200 rpm (predicted 0.008) Surface roughness reduced from 0.401 µm (base oil) to 0.098 µm at optimum condition	0.8 wt%	[52]
CuO & Al_2O_3	PAO 8 &SAE 75W-85	0.5, 1.0, 2.0 wt%	<50 nm	Homogeniser, water bath	10 min, 3 hr	Optimol SRV 4	200 N	50 Hz	25 °C, 2hr	CuO/PAO 8: COF ~0.11–0.13 (stable, Fig. 6b). Al_2O_3/PAO 8: COF increased above baseline ~0.15–0.18 CuO: WSD decreased up to 14% at 2 wt% PAO 8. Al_2O_3: WSD increased — abrasive damage	2 wt% CuO	[48]
TiO_2	SAE 20W 40	1.5 wt%	10–25 nm	Ultrasonic shaker		Pin-on-disc	40, 60, 90 N	0.5, 1.0, 1.5 m/s	5 min	COF ~0.05–0.07 at 1.5 wt% and 1.5	1.5 wt%	[53]

Nanolubricant details						Test Parameter				Results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Temp. and duration	Wear and Friction Reduction	Optimum Conc.	Ref.
										m/s (approx., from reported 50% reduction vs base oil ~0.10–0.14) wear values not reported numerically		
SnO_2	PAO	0.5 to 5 wt%	22-43nm	Ultrasonic homogeniser	5 min	UMT-3	25 N	1Hz	Room temp., 6 min	COF at 5 wt% SnO_2: ~0.097 (65.4% reduction from base oil COF = 0.28). COF at 1 wt%: ~0.11 Wear volume loss: base oil ~0.015 mm^3/m; 0.5 wt% SnO_2: ~0.0085 mm^3/m (43.7% reduction). 5 wt% SnO_2: highest wear loss ~0.013 mm^3/m	5 wt%	[54]

Although metal oxide nanoparticles have shown promising tribological behaviour in a number of studies, several practical limitations restrict their use as lubricant additives. A major challenge is their tendency to agglomerate within the base oil, especially at higher concentrations, which reduces their effective involvement at the sliding interface and can even lead to increased friction and wear. In addition, some metal oxide nanoparticles, are harder than the contacting metal surfaces, causing them to act as abrasive particles rather than protective additives and resulting in accelerated surface damage and larger wear scars.

1.5.3.3 Metal Sulfides Nanoparticles

Molybdenum disulfide (MoS_2) has long been recognised as one of the most effective lubricant additives due to its outstanding tribological properties. Recent studies have demonstrated that nano-sized MoS_2 exhibits superior friction-reducing performance compared to its micro-sized counterpart, primarily due to its smaller particle size, which enhances penetration into contact zones and promotes uniform film formation [55]. In addition to MoS_2, other metal sulfides such as tungsten disulfide (WS_2), iron sulfide (FeS), and copper sulfide (CuS) have also been used as friction-reducing additives. For example, FeS nanoparticles within the size range of 20–200 nm have been investigated as engine oil additives, with results indicating a significant reduction in COF, upon their incorporation [56]. Further research has explored the use of fullerene-like nanoparticles (IF) of sulfides, such as IF-MoS_2 and IF-WS_2, in synthetic base oils like polyalphaolefin (PAO). These studies revealed considerable improvements in tribological performance, attributed to the diffusion of sulfur atoms into the near-surface region, forming an S-enriched layer that facilitates friction reduction on the contact interface [57]. More studies on metallic sulfides are shown in the Table 1-4.

Table 1-4 Metal sulfides nanoparticles with testing conditions and results

Nanolubricant details						Test Conditions				Test results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Temp. & duration	Wear and Friction Reduction	Optimum Conc.	Ref.
FeS	API SL/CF 10W-40	0–2%	20–200 nm	Stirring & ultrasonication		Pin-on-disc	50 or 150 N	150 rpm	Room temp.; 20 min	Friction reduced to 0.018 and 0.024 at various loads. COF reduced from 0.08 → 0.018 (50 N) and 0.13 → 0.024 (150 N) at 2 wt%. Worn surface smoother with FeS; S diffusion layer ~10 µm confirms durable anti-friction layer.	2 wt%	[56]
MoS_2	Coconut oil & paraffin oil	0.25, 0.5, 0.75, 1%	90 nm	Ultrasonic shaker	1 h, 50°C	Pin-on-disc, Four-ball tester	2 to 4 MPa, 392 N	0.47 to 1.414 m/s, 600 rpm	75 ±2 °C, 60 min	Optimum COF: coconut oil 0.049 (surf.mod.) vs. 0.092 base; paraffin oil 0.066 (surf.mod.) vs. 0.099 base. Wear scar diam.: coconut 0.45 mm vs. 0.71 mm base; paraffin 0.54 mm vs. 0.78 mm base.	0.53% and 0.58% respectively	[58]

Nanolubricant details						Test Conditions				Test results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Temp. & duration	Wear and Friction Reduction	Optimum Conc.	Ref.
	SE15W40	0.1, 0.5, 1.0, 2.0 & 5.0 wt%	~50 nm	Homogenizer	30 min	Disc-on-disc	1500 N	500 rpm	Ambient, 180 s	COF reduced and stabilised for M1 (1 wt%) and M2 (2 wt%) samples after ~80 s. Surface roughness fell from ~4 μm (before) → <1 μm (M1).	≥1 wt%	[59]

Sulfide additives contain sulfur and, in some cases, molybdenum, both of which are regulated under modern low-SAPS engine oil standards that are designed to protect catalytic aftertreatment systems. As a result, using these additives as direct replacements for conventional anti wear additives such as ZDDP presents significant environmental and regulatory challenges.

1.5.3.4 Rare-earth Compounds

Rare-earth compounds have been extensively investigated in tribology for their potential application as lubricant additives. These materials can be utilised either in their pure form or as dopants within other nanoparticles, such as titanium dioxide (TiO_2), to enhance tribological performance. Their lubrication mechanisms are broadly similar to those of other nanoparticle additives, primarily involving the formation of tribofilms or adsorption layers on the contact surfaces.

Several rare-earth compounds, including cerium orthovanadate ($CeVO_4$), lanthanum hydroxide ($La(OH)_3$), cerium oxide (CeO_2), and lanthanum fluoride (LaF_3), have been widely studied as friction modifiers in lubricants. Research findings indicate that rare-earth compounds can significantly improve tribological properties by increasing load-carrying capacity by 10%–100%, extending lubricant life, and enhancing anti-wear performance of machine components. These improvements are accredited to their ability to form stable protective films and modify surface chemistry under boundary lubrication conditions.

Nano-lubricants based on rare-earth compounds are listed in Table 1-5.

Table 1-5 Rare earth compounds nanoparticles with testing conditions and results

Nanolubricants						Test Conditions				Test results		
Nanoparticle	Base oil	Concentration	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Temp. and duration	Wear and Friction Reduction↓	Optimum Conc.	Ref.
(LDH)-La-doped Mg/Al	CD 15W-40	0.5 g LDH/ 100 mL oil	185.96 nm	Ultrasonic bath	80 °C	Four ball tester	392 N	1200 rpm	RT, 60 min	Reduction in wear 12.9% and friction to 0.093	n/a	[60]
LaF_3	Fluoro silicon oil	0.02, 0.04, 0.06, 0.08 & 1.0 wt%	10–30 nm	n/a	n/a	Four ball tester	300 N	1450 rpm	25 °C, 30 min	Friction and wear decreased ↓ until 1 wt% concentration	0.08 wt%	[61]
Stearic acid-capped/$CeBO_3$	Rapeseed oil	2.0 wt%	8 nm	n/a	n/a	Four ball tester	392 N	1500 rpm	Room temp	Friction and wear decreased ↓	n/a	[62]
CeO_2	Lithium grease	0.2, 0.4, 0.6, 0.8 & 1.0 wt%	<500 nm	Ultrasonic dispersion	20 min	Four ball tester	392 N	1200 rpm	75 °C, 60 min	Wear ↓13%, friction ↓28%	0.6 wt%	[63]
	Titanium complex grease	2 wt%	<10 nm	n/a	n/a	Four ball tester	392 N	1450 rpm	25 °C, 10 s; 75 °C, 60 min	Improved	2 wt%	[64]

1.5.3.5 Carbon-based Additives and Reinforcements

Over the past decade, extensive research has been engaged on metals, metal oxides, and transition metal dichalcogenides (TMDs), for example molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), as additives in liquid-based lubricants. Their effectiveness is primarily attributed to the inherent low-shear properties of their basal planes, which facilitate friction reduction under boundary lubrication conditions. In addition to TMDs, inorganic fullerenes (IFs) have emerged as another promising class of nano-additives, characterised by their spherical or tubular structures. Particular attention has been directed towards fullerene-like MoS_2 and WS_2 (IF-MoS_2 and IF-WS_2) owing to their demonstrated ability to reduce friction and wear significantly [65]. Despite these advantages, metal-based nano-additives and TMDs present environmental concerns, primarily due to their sulfur content and the potential release of metallic nanoparticles into the environment [37]. Furthermore, issues related to toxicity, complex synthesis procedures, and high production costs put significant challenges to their widespread acceptance. Long-term use of these solid oil additives may also lead to performance degradation, limiting their practical applicability.

In response to these limitations, recent research has increasingly focused on carbon-based nanomaterials, for instance, graphene, carbon nanotubes (CNTs), and fullerenes, that offer unique structural and tribological properties without the environmental drawbacks associated with sulfur-containing compounds [66]. A comprehensive review of carbon-based lubricant additives and their tribological performance is presented in Table 1-6.

Table 1-6 Carbon based additives and nanoparticles with testing conditions and results

Nanolubricant						Test Conditions				Results		
Nanoparticles	Base oil	Amount	Particle size	Dispersion Method	Duration & Temp.	Tribometer type	Load	Speed	Temp.& duration	Wear and Friction Reduction	Optimum Conc.	Ref.
Cu And Cu/Gr	5W-30	0.03–0.6 wt%	5-10 µm	Oleic acid (OA), mechanical stirring	4 h	Piston ring/liner reciprocating tribometer	90 to 368 N	0.154 to 0.6 m/s	n/a	Friction and wear reduced (26.5-32.6% and 25-30%)	0.5 wt%	[67]
Nanodiamond	Hydraulic oil	1 wt%	2 µm	Magnetic stirrer, Ultrasonic mixing	30 min, 1 hr, 50 °C	Ball-on-disk	3 N	1.2–38.4 mm/s	25–125 °C	High and unstable tribological properties	1 wt%	[68]
	PAO	0.2–0.8 wt%	60–90 nm	Ultrasonic probe	30 min	Ball-on-disk	100 N	0.58 m/s	n/a	Higher concentration increased wear and friction	0.2 wt%	[69]
	Paraffin oil	0.025–5 wt%	110 nm	Ultrasounds	30 min	Ball-on-ring	50–300 N	500 rpm	Room temp, 60 min	Wear ↓23.73%, COF ↓14.77%	0.2 wt%	[70]
	CPC R68 commercial oil	1–3 vol%	4.37±0.45 nm	Stirring, supersonic redispersed	1 h, 60 °C	Blocks-on-ring		4.87–7.30 m/s	Room temp, 60 min	Wear and friction decreased	n/a	[71]
Graphite carbon nanosphere	500SN base oil	0.2 wt%		Stirring	n/a	Ball-on-disk	100 N	25 Hz	50 °C	Significantly reduced	0.2 wt%	[72]
Graphite	Base oil	1–4 wt%	55 nm	Ultrasonic probe	35 min	Four-ball tester	392, 588 & 784 N	1200 rpm	75 °C, 1 h	Wear and friction decreased	3 wt%	[73]

1.5.3.6 MXenes and MXenes based Nano additives

Among different nanomaterials, MXenes have gained significant attention due to their exceptional low shear properties[80], graphene-like lamellar structure and good mechanical strength [81]. MXenes are members of 2D layered transition metal nitrides, carbides and carbonitrides based on the MAX phase [82]. Single flakes MXenes are denoted by the chemical formula $M_{n+1}X_nT_x$ [83] where M: stands for early transition metals groups 3-6 of the periodic table [84], X: stands for C or N with n = 1−4, and T_x: stands for surface termination groups of -O, -OH, -F, and/or -Cl [85].

MXenes exhibit remarkable versatility, enabling their application across multiple domains, including lithium-ion batteries, biosensors, supercapacitors, and nano-adsorption technologies, with their performance largely governed by surface functional groups [86]. Their unique combination of properties: graphene-like layered structure, self-lubricating capability, tribofilm formation potential, and high mechanical strength, makes MXenes highly suitable for tribological applications [87]. These characteristics allow MXenes to function as advanced friction modifiers, offering environmentally compliant alternatives to traditional additives.

A summary of recent studies investigating different MXene types for friction and wear reduction is presented in Table 1-7.

Table 1-7 MXene with details of testing conditions and results

MXene Additive	Base Lubricant	Additive Size & Loading	Dispersion Method	Tribometer type and Test Conditions	Friction & Wear Improvement	Optimum Conc.	Ref.
$Ti_3C_2(OH)_2$ MXene (multilayer nanosheets)	100SN mineral base oil	Up to 1.0 wt% (10–20 nm thick flakes)	Ultrasonic exfoliation (HF etch) and direct oil dispersion	Ball-on-disk (UMT-2), 15 N load, 200 rpm, room temp, ~30 min	COF ↓ ~20% (vs. neat oil under 15 N); wear data not reported	~1.0 wt% (higher wt% gave no further benefit)	[88]
Ti_3C_2Tx/MoS_2 Heterostructure	150N mineral oil	0.3 wt% (few-layer Ti_3C_2 with MoS_2)	In-situ hydrothermal growth	Ball-on-disk, 50 N, 0.1 m/s, 75 °C, 30 min	COF ↓ 39%, wear ↓ 85%	0.3 wt%	[89]
MXene/HS Composite	PAO10 synthetic oil	1.0 wt% (Ti_3C_2/metal-hydroxide composite)	Hydrothermal growth, direct dispersion	Four-ball, 200–350 N, 1200 rpm, 75 °C, 60 min	COF ~0.12; wear ↓ 82%	1.0 wt%	[90]
MoS_2@Ti_3C_2 MXene Hybrid	SAE 5W-40 engine oil	0.05 wt% (few-layer Ti_3C_2 decorated with MoS_2)	Microwave-assisted synthesis	Four-ball, 40 kgf, 1200 rpm, 75 °C, 1 h	COF ↓ 13.9%, wear ↓ 23.8%	0.05 wt%	[91]

1.6 Factors Affecting the Tribological Properties of Nanoparticles

Several parameters critically influence the performance of nanoparticles when employed as lubricant additives within a lubricating system. These include particle size, size distribution, particle shape, agglomeration state, structural characteristics and crystallinity, chemical composition, porosity and surface area, and surface functionality. These factors play a significant role in determining the nanoparticles' ability to penetrate contact zones, form protective tribofilm, and maintain stability under operating conditions. An illustration of these influencing parameters is presented in Figure 1-3. In the subsequent part of this section, selected factors are discussed in detail to elucidate their impact on tribological behavior.

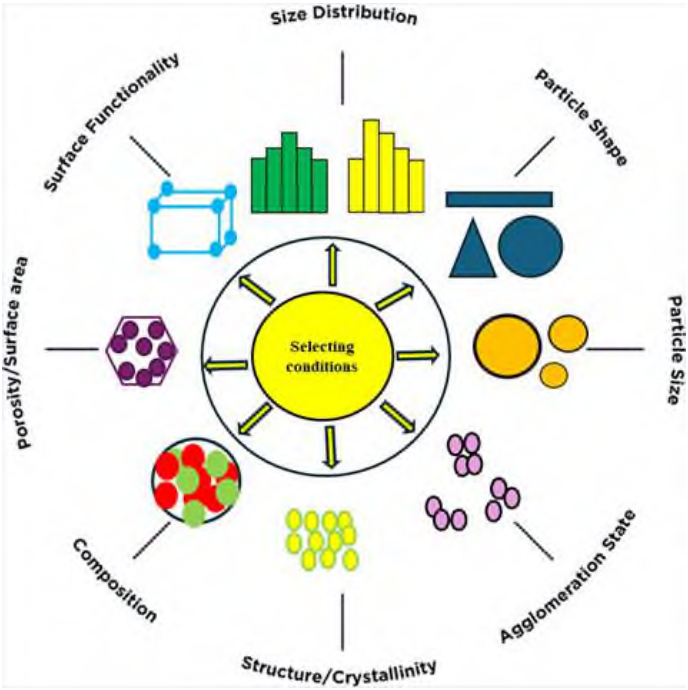

Figure 1-3 Schematic illustration of factors affecting nanoparticle performance [92].

1.6.1 Morphology of Nanoparticles

The morphology or shape of nanoparticles is an essential consideration when preparing nano lubricants, as it is a relevant parameter during loading. Researchers have identified five types of nanoparticle forms: Onion-like, Granular, Spherical, Sheet, and Tube type.

Statistics for the nanoparticle morphology are shown in Figure 1-4[38]. According to these statistics, approximately 57% of nanoparticles exhibit a spherical shape, followed by sheet-like, granular, onion-like, and tubular forms.

Spherical nanoparticles are particularly advantageous in lubrication applications because they act as nanoball bearings, promoting rolling between frictional surfaces. This rolling effect reduces shear stress and enhances load-bearing capacity, resulting in improved friction and wear performance. For instance, studies have shown that spherical nano-Al_2O_3 significantly improves friction reduction, wear resistance, and load-carrying capability through the ball-bearing mechanism [93].

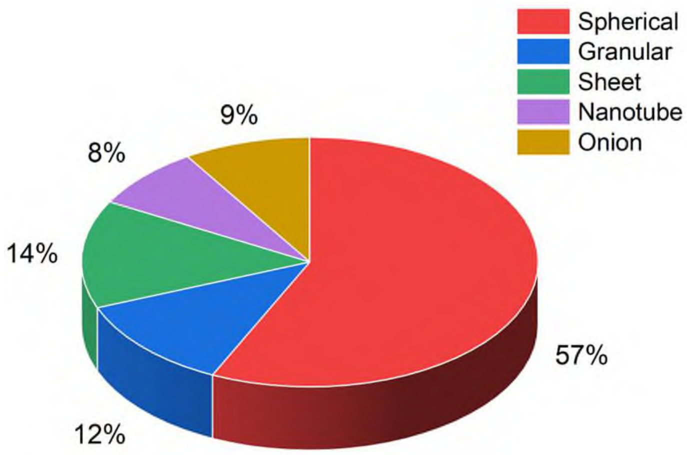

Figure 1-4 Statistics of the nanoparticles morphology [38].

1.6.2 Concentration of Nanoparticles

Similar to nanoparticle morphology and size, the concentration of nanoparticles is a critical parameter influencing the performance of nano lubricants. Optimal concentration ensures effective dispersion, minimises agglomeration, and maximises tribological benefits without causing detrimental effects such as increased viscosity or abrasive behaviour. Zhang et al. [94] investigated the effect of varying concentrations of Sn and Fe nanoparticles in base oil at 0.1, 0.5, and 1.0 wt%. Their tribological experiments revealed that the optimum concentration for both nanoparticles was 1.0 wt%. However, the functional performance differed: Fe nanoparticles were more effective in reducing wear, whereas Sn nanoparticles exhibited superior friction-reducing capability.

Koshy et al. [58] examined the tribological behavior of coconut oil and paraffin oil blended with different concentrations of MoS_2 nanoparticles. Their findings indicated that the optimum concentration of MoS_2 was 0.53 wt% for coconut oil and 0.58 wt% for paraffin oil, highlighting that the ideal concentration is strongly dependent on the base oil chemistry. These results underscore the importance of determining the optimal concentration for any additive combination to achieve maximum tribological performance. Failure to optimise concentration can lead to diminished effectiveness or even adverse effects on friction and wear behaviour.

1.6.3 Influence of Nanoparticle Size on Tribological Performance of Nano lubricants

Numerous studies have demonstrated that nanoparticle size is a critical parameter significantly influencing the tribological behaviour of nano lubricants. Smaller nanoparticles exhibit a greater tendency to become entrained within the tribological contact interface, thereby enhancing their functional effectiveness. Typically, the characteristic size of nanoparticles is defined as the thickness of a lamellar structure or the diameter of a tubular or spherical particle, generally less than 100 nm.

The tribological properties of nanoparticles are inversely affected by their size, primarily due to variations in surface-to-volume ratio, which governs the reaction kinetics [95]. For nanoparticles with dimensions of approximately 100 nm or larger, hardness tends to increase as particle size decreases. Conversely, when particle size falls below 10 nm, further size reduction results in softer nanomaterials. If the hardness of nanoparticles exceeds that of the tribo-pair materials, surface damage such as scratches and indentations may occur [96]. Therefore, both size and hardness are crucial considerations, as excessively hard nanoparticles such as nano-Al_2O_3, can induce abrasive wear and promote re-agglomeration within the base oil [48].

Operating conditions and the optimisation of nanoparticle size are strongly correlated with the tribological performance of nano lubricants. Experimental findings indicate that smaller $CaCO_3$ nanoparticles (approximately 30 nm) deliver superior tribological performance under high-load and low-frequency conditions, whereas larger particles (50–80 nm) exhibit moderate performance at higher frequencies [97]. Similarly, another study reported that under low-frequency conditions, smaller SiO_2 nanoparticles (around 40 nm) provide optimal friction-reducing capability, while larger SiO_2 particles (approximately 90 nm) demonstrate improved performance under high-frequency conditions [98].

1.7 Major Lubrication Mechanism

According to tribological theory, under mixed or boundary lubrication regimes, nanoparticles contribute to the formation of a tribofilm layer through deposition processes within the lubricating system. Extensive research has been undertaken to elucidate the mechanisms by which nanoparticles reduce friction and wear in such systems. When incorporated into lubricants, nanoparticles not only mitigate friction and wear but also enhance the load-bearing capacity of interacting machine components.

Dispersed within the base oil, nanoparticles improve tribological performance primarily through four distinct mechanisms, as illustrated in Figure 1-5:
(a) **Rolling mechanism** – nanoparticles act as nano-sized rolling elements, reducing shear stress at the contact interface;
(b) **Mending mechanism** – nanoparticles fill surface asperities and micro-cracks, restoring smoothness;
(c) **Polishing mechanism** – nanoparticles abrade and refine rough surfaces, decreasing surface irregularities;
(d) **Protective film formation** – nanoparticles deposit on contact surfaces, creating a tribofilm that prevents direct metal-to-metal contact.

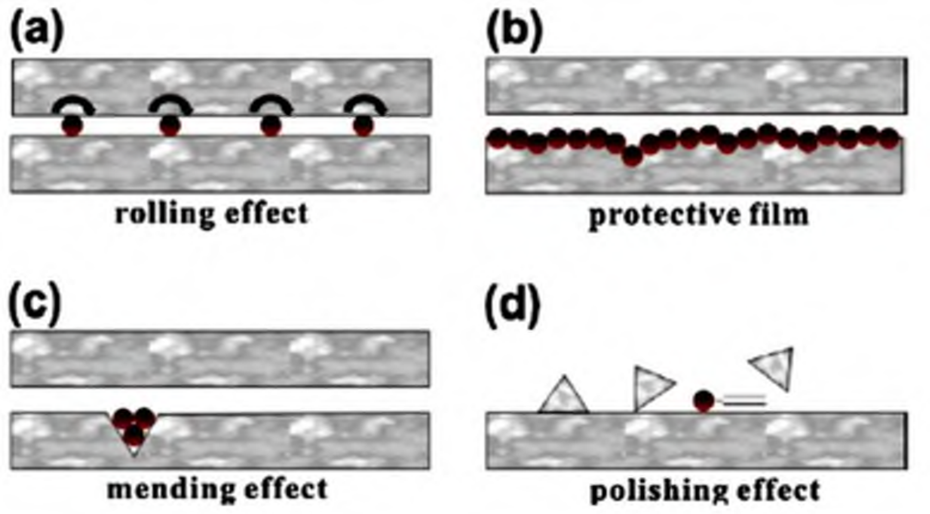

Figure 1-5 Possible mechanism of lubrication for nanoparticles as friction modifier to improve tribological performances: a) rolling effect, b) protective film mechanism, c) mending effect, d) polishing effect [99].

The effectiveness of lubrication mechanisms is governed not only by the intrinsic properties of the base oil and nanoparticles but also by the prevailing operating conditions. Key parameters such as applied load, temperature, sliding velocity, and the surface roughness of the contacting materials significantly influence the dominant lubrication mechanism [100]. The mechanisms are discussed below:

1.7.1 Rolling Mechanism

The rolling mechanism is characterised by the absence of mechanical or chemical reactions within the lubricating system. In this process, spherical nanoparticles act as nano-sized rolling elements between frictional surfaces, converting pure sliding friction into a mixed sliding–rolling regime. This transformation significantly reduces shear stress at the contact interface, thereby lowering frictional losses. Several factors govern the efficiency of this mechanism, including the shape of the nanoparticles, the type and magnitude of applied load, and the hardness of the tribo-pair materials. At relatively low loads, spherical nanoparticles maintain their structural rigidity and resist deformation, which facilitates effective rolling and contributes to friction reduction [95].

Abdullah et al. [101] conducted an extensive investigation into the tribological behavior of surface-modified hexagonal boron nitride (h-BN) and aluminium oxide (Al_2O_3) nanoparticles. These nanoparticles were treated with oleic acid and blended with SAE 15W40 oil. Tribological tests were performed using a four-ball tester, where the balls were composed of chromium steel. The results revealed that h-BN nanoparticles exhibited outstanding anti-friction and anti-wear properties, improving wear resistance by 58% compared to the base oil. In contrast, Al_2O_3 nanoparticles demonstrated a detrimental effect on wear performance. The authors attributed these findings to the "ball-bearing effect," wherein nanoparticles function as rolling elements, reducing both the coefficient of friction (COF) and wear rate [101].

Zhao et al. [102] successfully synthesised a sandwich-like Mn_3O_4/graphene (Mn_3O_4/G) nanostructure by reutilising graphene oxide impurities of Mn^{2+} ions. Remarkably, even at elevated temperatures and ultralow concentrations, Mn_3O_4/G exhibited superior tribological performance. This enhancement was attributed to the synergistic lubrication effect between Mn_3O_4 nanoparticles and graphene nanosheets, facilitated by combined "slide–roll" interactions. Such hybrid structures demonstrate the potential for advanced lubrication strategies under extreme operating conditions.

1.7.2 Mending Mechanism

In the mending mechanism, nanoparticles are deposited onto the contacting surfaces to form a physical tribofilm that compensates for material loss caused by wear (Figure 1-6). This process is often referred to as a self-repairing mechanism, as it restores surface integrity by filling scars, grooves, and micro-cracks. The deposition of nanoparticles within these surface defects improves the overall surface properties and mitigates further deterioration. To characterise this mechanism, Energy-Dispersive X-ray Spectroscopy (EDX) has been widely employed, providing elemental analysis of the tribofilm formed during lubrication. Wang et al. [103] reported a pronounced self-repairing effect using a graphene/silver (Ag) nanocomposite. Their findings confirmed that the nanocomposite effectively deposited on worn surfaces, forming a protective layer that compensated for mass loss and enhanced tribological performance.

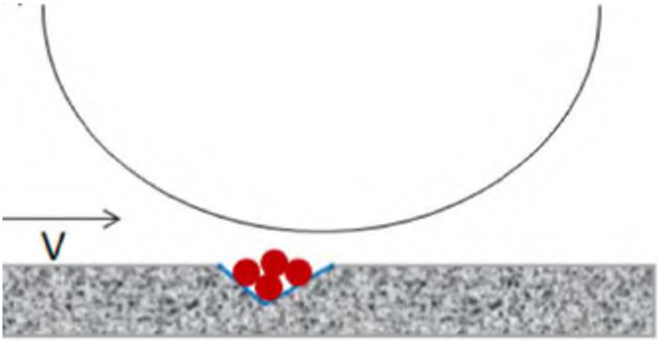

Figure 1-6 Schematic illustration of mending mechanism.

Ahmadi et al. [104] investigated the tribological performance of various nano additives, including carbon nanoballs, fullerene nanoparticles, and vanadium oxide nanotubes dispersed in SAE 20W50 engine oil. Their results demonstrated that the nano lubricant exhibited superior anti-wear properties compared to the base oil. Among the tested additives, vanadium oxide nanotubes produced the smallest wear scar diameter, which was attributed to their exceptional ability to cover and protect the rubbing surfaces, thereby reducing material loss.

Similarly, Srinivas et al. [105] examined the tribological behaviour of surface-modified molybdenum disulfide (MoS_2) nanoparticles dispersed in SAE 20W40 oil using a standard four-ball tester. Their evaluation included friction, wear, and extreme pressure properties. The addition of MoS_2 at a concentration of 0.5 wt% resulted in a 16.4% reduction in the coefficient of friction (COF). Based on their observations, the researchers concluded that the predominant lubrication mechanism operating on the tribo-pairs was the mending mechanism, wherein nanoparticles deposit into surface defects, restoring smoothness and enhancing wear resistance.

1.7.3 Polishing Mechanism

The polishing mechanism represents another significant surface enhancement process; wherein surface roughness is reduced through nanoparticle-assisted abrasion. Research indicates that the degree of surface refinement correlates closely with the size of the nanoparticles employed (Figure 1-7). In this mechanism, the hardness of the nanoparticles plays a pivotal role in friction reduction. Nanoparticles with higher hardness abrade surface asperities, thereby smoothing the contact interface. For this reason, the process is often referred to as artificial smoothing.

Lee et al. [106] evaluated the influence of various nanoparticles including copper, copper oxide, fullerene, and multi-walled carbon nanotubes (MWCNTs), when dispersed in mineral oil. Their findings revealed that the coefficient of friction (COF) in nanofluids was consistently lower than that of the base oil alone. The reduction in friction was attributed to the polishing effect of nanoparticles, which effectively removed surface asperities and improved smoothness. Similarly, Ignole et al. [107] reported that titanium dioxide (TiO_2) nanoparticles, in both rutile and anatase phases, acted as polishing agents on contacting surfaces, thereby reducing friction through surface refinement.

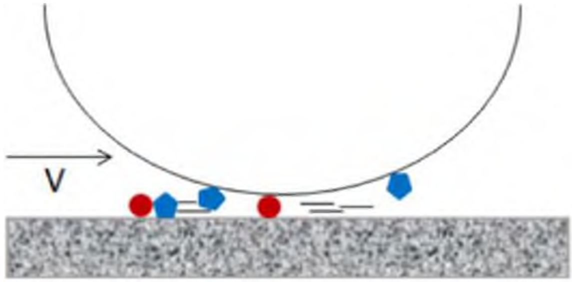

Figure 1-7 Schematic illustration for polishing mechanism [107].

1.7.4 Protective Film Mechanism

Friction and wear can be significantly reduced through the formation of a thin protective film on the contacting surfaces, resulting from the interaction between nanoparticles and the frictional interface (Figure 1-8). This tribofilm acts as a barrier that prevents direct metal-to-metal contact, thereby improving lubrication efficiency. Researchers have reported that this mechanism provides excellent lubrication performance and is highly effective in reducing both friction and wear. Under specific lubricating conditions, the protective film is generated through chemical reactions between the nanoadditives and the surface material. These reactions lead to the formation of a stable layer that enhances tribological properties by reducing asperity interaction and improving load-bearing capacity. The effectiveness of this mechanism depends on factors such as nanoparticle composition, concentration, operating temperature, and the chemical affinity between the additive and the substrate.

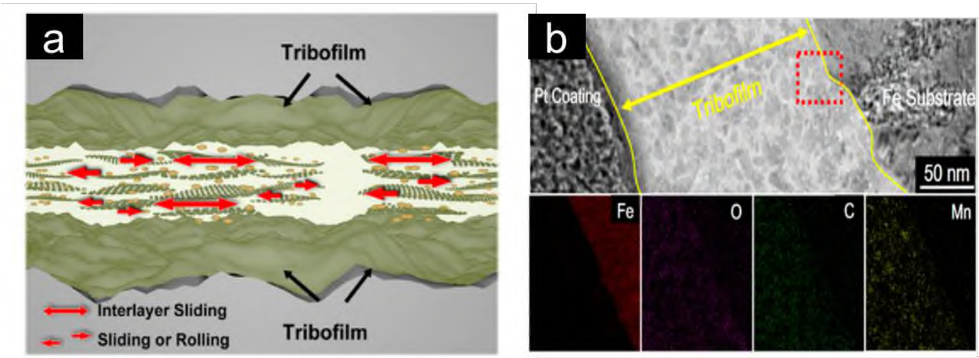

Figure 1-8 a) Schematic illustration of the lubrication mechanism of Mn_3O_4/G. b) TEM image of the cross-section of the tribofilm lubricated by Mn_3O_4/G by FIB. The element mapping data of Fe, O, C, and Mn were for the red area of tribofilm [102].

The hardness and chemical reactivity of nanoparticles play a crucial role in the formation of protective films. Softer nanoparticles can more readily generate a tribofilm through melting under operating conditions, whereas harder nanoparticles typically rely on chemical interactions with the surface. Alves et al. [108] conducted a comparative study by dispersing CuO and ZnO nanoparticles in different base oils, including synthetic oil (PAO), mineral oil, and vegetable oils (sunflower and soybean oils). Their findings revealed that nanoparticles were effective only in petroleum-based oils. Although vegetable oils exhibited lower friction coefficients compared to synthetic and mineral oils, oxide nanoparticles did not enhance the tribological properties of sunflower or soybean oils. This limitation was attributed to the presence of polar groups in vegetable oils, which hindered the formation of a stable protective film. Conversely, ZnO nanoparticles mixed with mineral oil significantly reduce friction and wear by forming a tribofilm on the contact surfaces. These observations underscore that the effectiveness of nanoparticles in protective film formation is strongly influenced by the chemical structure of the base oil.

Further insights were provided by Zhou et al. [109], who investigated steel–steel tribological contacts lubricated with base oil, both with and without phosphonium–phosphate ionic liquid (IL). They proposed a multi-step tribofilm formation process involving wear debris generation and fragmentation, direct surface reactions, mechanical deposition through mixing and pressing of wear debris, chemical deposition, and tribo-chemical reactions between reactive elements and wear debris. Additionally, oxide interlayer growth was facilitated by oxygen diffusion. The resulting tribofilm structure is illustrated in Figure 1-9.

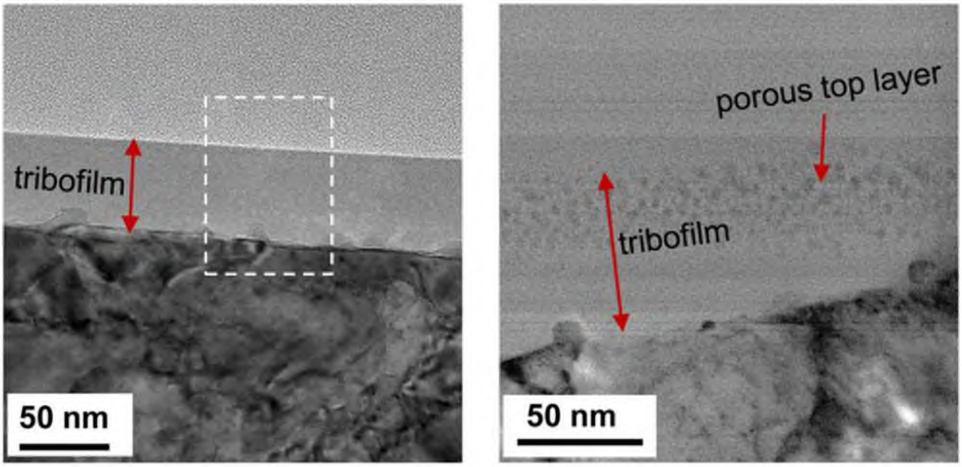

Figure 1-9 Tribofilm formed in the ionic liquid-containing oil (a) amorphous structure and a two-layered structure which includes a porous top layer entrenched with nanoparticles and an amorphous bottom layer [109].

1.8 Nano Structures of Tribofilm

During sliding contact, the formation of a tribofilm is essential for preventing direct metal-to-metal interaction and reducing friction. However, the thickness of this tribofilm plays a critical role in its effectiveness. A thin tribofilm at the nanoscale is generally preferred over a thicker layer. This is because a dense tribofilm with a large coverage area is more susceptible to stress concentration under repeated extrusion during sliding. Such stress accumulation can lead to crack initiation within the film. Consequently, tribofilm flakes may form and peel off due to the shear forces generated by friction, ultimately detaching from the contact surface [110]. In contrast, a thin tribofilm provides better durability and stability under dynamic loading conditions.

A study investigated the tribological behavior of multi-walled carbon nanotubes (MWCNTs) and MWCNT/nano-ZrO_2 hybrid nanoparticles compounded into a non-asbestos brake material. When only MWCNTs were incorporated, a uniform single-layer tribofilm was formed with a thickness of approximately 250–300 nm. Interestingly, when nano-ZrO_2 was added alongside MWCNTs, a double-layer tribofilm of similar thickness was observed.

In all tribofilm layers, numerous short-range graphitic nanograins, only a few nanometers in size, were embedded within the structure, maintaining a lattice spacing of 0.32 nm. These nanograins were formed through the conversion of carbon nanotubes, facilitated by the presence of oxygen atoms in the surrounding atmosphere. This structural transformation contributed to the tribofilm lubricating properties and its ability to withstand high contact stresses as shown

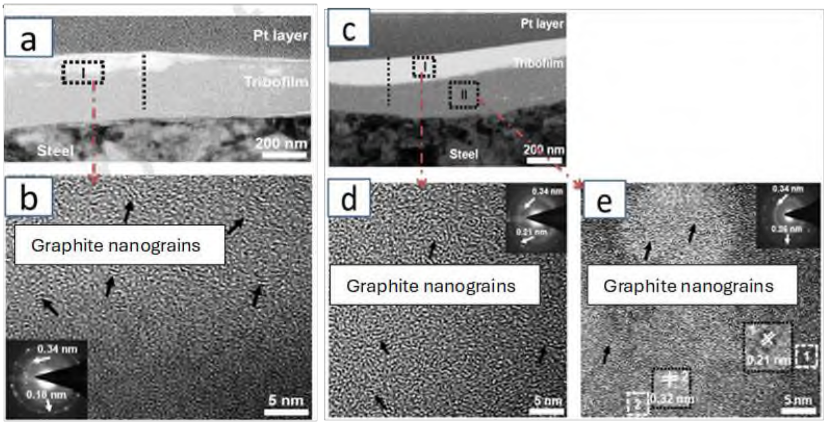

Figure 1-10 HR-TEM image of the Nano structure of tribofilm using MWCNTs (a)(b), Nano structure of tribofilm using MWCNTs/ZrO2 (c)(d)(e) [111].

Recent studies have revealed the presence of nanoparticle-encapsulated tribofilm structures during tribological processes. Ma et al. [112] investigated the tribological mechanisms of nanocomposite self-lubricating coatings embedded with in-situ synthesised Ag_2S nanoparticles. High-resolution transmission electron microscopy (TEM) analysis confirmed that the tribofilm formed during sliding was highly uniform, with an average thickness of approximately 96 nm, as illustrated. Furthermore, individual Ag_2S nanoparticles exhibited distinct lattice fringes with a spacing of 0.221 nm, corresponding to the interlayer spacing of the (031) crystallographic plane.

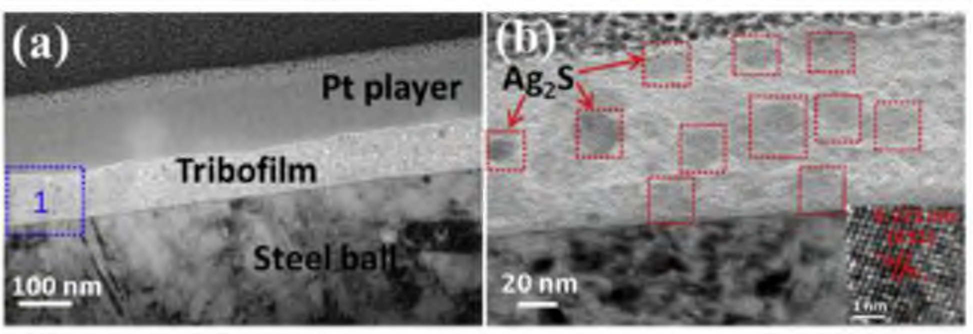

Figure 1-11 (a) TEM image of cross-section of tribofilm (b) HR-TEM image of the entrapped single Ag_2S nanoparticle in region 1 of the tribofilm [112].

During frictional contact, Ag_2S nanoparticles penetrated the interface and became entrapped within the tribofilm due to the combined influence of normal and shear forces. These embedded nanoparticles played a critical role in enhancing both the load-carrying capacity and the structural stability of the tribofilm. This encapsulation phenomenon demonstrates the synergistic effect of nanoparticles in reinforcing tribofilms, thereby improving overall tribological performance under demanding operating conditions.

1.9 Selection of Nanoparticles as Lubricant Additive

Among the wide range of nanoparticles explored as lubricant additives, including graphene, graphite, metal oxides, MoS_2, and carbon nanotubes, nanodiamonds have emerged as particularly promising candidates due to their distinctive combination of mechanical, thermal, and surface chemical properties. There are tribological advantages of nanodiamonds compared with competing nanoparticles, with particular emphasis on their structural compatibility with diamond like carbon coatings and their synergistic potential when combined with organic friction modifiers such as glycerol monooleate.

The primary advantage of nanodiamonds lies in their exceptional hardness, which enables lubrication mechanisms that softer additives cannot provide. Xu et al. [74] were among the first to show that detonation synthesised nanodiamonds dispersed in paraffin oil can penetrate the contact interface, embed into softer metallic surfaces, and form a durable boundary layer that supports load while reducing friction and wear. Their near spherical shape also enables a rolling action at the interface, partially converting sliding friction into rolling friction. This ball bearing effect was later confirmed by Peng et al. [70], who reported friction reductions of up to 14.77 percent and wear scar diameter reductions of approximately 23.73 percent in liquid paraffin at optimal concentrations of 0.2 to 0.5 wt%. Raina and Anand [69] extended these findings to polyalphaolefin base oil, observing an 8.34 percent reduction in coefficient of friction and around a 27 percent reduction in wear volume at 0.2 wt%. Importantly, SEM analysis showed a transition in the dominant wear mechanism from severe adhesive delamination to mild abrasive ploughing, a characteristic behaviour of nanodiamond lubrication that has not been consistently achieved with graphene or graphite under comparable conditions.

By comparison, other nanoparticle additives tend to show more limited or condition dependent performance. Metal oxide nanoparticles such as CuO and TiO_2 primarily reduce wear through tribochemical film formation[75], a mechanism that depends strongly on temperature and lubricant chemistry and is therefore less reliable across varying operating conditions. MoS_2 nanosheets are effective under extreme pressure conditions but are chemically reactive in oxidative or high humidity environments [76], which limits their long-term durability. In contrast, nanodiamonds are chemically inert across the typical operating temperature range of lubricants, allowing them to maintain consistent performance without the degradation risks associated with these alternatives.

Another reason for selecting nanodiamonds as lubricant additives is their strong structural and chemical compatibility with diamond like carbon coatings, which are increasingly applied to engine components such as piston rings, camshafts, and valve train elements. DLC coatings consist of amorphous carbon containing both graphitic and diamond bonded carbon, and their tribological behaviour under boundary lubrication is strongly influenced by lubricant chemistry. Erdemir et al. [77] showed that carbon rich tribofilm derived from lubricating oils play a critical role in maintaining very low friction on DLC surfaces and that carbon-based additives accelerate the formation of the protective films. The combination of nanodiamonds with organic friction modifier like glycerol monooleate could provide additional synergistic benefits. GMO reduces friction by forming ordered molecular layers on metal surfaces through adsorption of its polar head group [11], but these layers become unstable at high temperature and load. Nanodiamonds compensate for this limitation by providing mechanical load support when the molecular film breaks down, preventing direct asperity contact. At the same time, GMO continues to reduce shear in mixed and boundary lubrication regimes. Ratoi et al. [32] showed that organic friction modifiers such as GMO are most effective when surface coverage is maximised, while Berman et al. [78] demonstrated that combining carbon based nanoparticles with molecular lubricant films produces greater friction and wear reduction than either component alone. In addition, the sp^3 carbon surface of nanodiamonds can be functionalised with carboxylic acid and hydroxyl groups [79], enhancing their affinity for GMO and promoting adsorption at the interface, leading to a more robust composite boundary film.

Overall, the available tribological evidence shows that nanodiamonds outperform other nanoparticle additives due to their unique combination of hardness enabled polishing, rolling action, chemical stability, and high thermal conductivity. Their structural similarity to the diamond bonded phase of DLC coatings makes them particularly well suited for modern coated engine components, avoiding the chemical incompatibilities associated with sulfur and phosphorus-based additives. When combined with glycerol monooleate, nanodiamonds could form a synergistic boundary lubrication system that could be well matched to the demanding conditions of modern internal combustion and electric drive systems.

Another promising nano additive known as MXene, are a family of two dimensional transition metal carbides and nitrides with the general formula $M_{n+1}X_nT_x$, first reported in 2011 [81]. Since that initial discovery, $Ti_3C_2T_x$ has become the most extensively studied MXene, while ordered double transition metal MXenes such as $Mo_2TiC_2T_x$ have emerged as distinct materials in which outer molybdenum layers sandwich an inner titanium carbide core [85]. Both $Ti_3C_2T_x$ and $Mo_2TiC_2T_x$ share a nanolaminate structure characterised by strong in plane bonding and weak interlayer interactions, giving rise to inherently low shear resistance [85]. From a mechanical perspective, $Ti_3C_2T_x$ is among the stiffest two dimensional materials, while $Mo_2TiC_2T_x$ is predicted to offer even higher strength due to the presence of molybdenum as the outer transition metal, making the two materials complementary for moderate and high load tribological applications[85].

In addition to favourable mechanical behaviour, both MXene offer tunable and chemically distinct surfaces that are highly advantageous for lubrication. Their surface terminations can be tailored during synthesis to influence dispersion stability, friction behaviour, and interfacial adhesion, with Mo based MXene tending to exhibit oxygen rich terminations that further reduce sliding energy barriers. $Ti_3C_2T_x$ already demonstrates strong tribological performance as an oil additive, solid lubricant coating, and nanofluid core, delivering large reductions in friction and wear and forming thick, protective tribofilms under severe conditions [85]. Although $Mo_2TiC_2T_x$ remains comparatively underexplored, its higher predicted strength, molybdenum driven tribochemistry, and structural stability under sliding suggest strong potential for demanding applications. Across both materials, a common lubrication mechanism is the formation of durable, self-lubricating tribofilms containing degraded MXene nanosheets and metal oxides that convert hard surface contacts into low shear interfaces and continuously replenish the lubricating layer. Together, these attributes explain why $Ti_3C_2T_x$ and $Mo_2TiC_2T_x$ are well suited for selection as lubricant nanoadditives, while also highlighting the need for further systematic study of oxidation stability, and double transition metal MXene systems.

Based on the research questions, the objective of this project is divided into four different parts and is briefly described.

1.10 Aim and Objective

The primary aim of this research was to develop environmentally sustainable lubricant additive formulations and to elucidate their behaviour within multi-additive systems based on synthetic base oils. The overarching goal was to minimise friction and wear while reducing dependence on conventional additives such as ZDDP and MoDTC, which contain sulfur and phosphorus and are associated with adverse environmental impacts. This objective involved either lowering or replacing the concentrations of ZDDP and MoDTC by incorporating alternative additives capable of forming protective tribofilm in situ to safeguard contacting surfaces.

Objective 1: Synergy of GMO, ND and ZDDP. This study aimed to investigate the tribological performance of an organic friction modifier (GMO) combined with nanodiamonds (NDs) in the presence of a low concentration of ZDDP under boundary lubrication conditions. To achieve this aim, the research set specific, measurable, and time-bound objectives. Pin-on-plate tribological tests were carried out using a synthetic base oil formulated with optimised concentrations of GMO, NDs and ZDDP to evaluate their combined effect on friction and wear. Friction coefficients and wear rates were quantified under varying temperatures and additive combinations, providing measurable outcomes. The study also included surface characterisation to examine tribofilm formation, ensuring that the objectives remained achievable within the experimental timeframe. These objectives were directly relevant to the broader goal of reducing or replacing ZDDP in lubricant formulations without compromising wear resistance. All experimental work and subsequent analysis were completed within the defined research schedule, ensuring that the objectives were time-bound.

Objective 2: Effectivity of Nanodiamonds with GMO and MoDTC. This part of the study investigated the effect of incorporating nanodiamonds (NDs) with an organic friction modifier (GMO) and molybdenum dithiocarbamate (MoDTC), alongside a low concentration of ZDDP. It explored a multi-additive lubricant system under reciprocating sliding conditions at two different temperatures to determine the potential for synergistic interactions that could minimise friction and wear beyond what individual friction modifiers achieve independently. The objective extended from a single-additive system to a multi-additive system to assess the feasibility of using such complex friction modifiers and whether they effectively reduced friction and wear. This provided a foundation for evaluating their role in advanced formulations and served as a bridge towards the introduction of MXene-based additives in future research.

Objective 3: Understanding the reactivity of $Mo_2TiC_2T_x$ MXene with GMO and ZDDP. This part of the study focused on evaluating the performance of Mo-based MXene ($Mo_2TiC_2T_x$) and determining its effectiveness as a lubricant additive when combined with GMO and a low concentration of ZDDP. Lubricant formulations were prepared using

$Mo_2TiC_2T_x$ nanosheets, GMO, and ZDDP at 0.2 wt%, followed by testing under reciprocating steel-on-steel sliding conditions. Subsequent surface characterisation techniques were employed to analyse tribofilm formation and wear mechanisms. The performance objective for this stage of the research was to achieve low friction and wear while utilising Mo-based MXene with GMO as a lubricant additive, compensating for the reduced ZDDP content in providing anti-wear protection. This enabled an evaluation of whether $Mo_2TiC_2T_x$ MXene could fulfil the goal of reducing friction and wear, thereby supporting its potential role in advanced lubricant formulations.

Objective 4: Investigating the synergy of $Ti_3C_2T_x$ MXene with Nanodiamonds and GMO. This part of the study investigated the synergy between $Ti_3C_2T_x$ MXene, nanodiamonds (NDs), and GMO, exploring two-dimensional MXene nanosheets as novel lubricant additives. The objective was to evaluate the tribological performance of $Ti_3C_2T_x$ MXene when incorporated alongside NDs and GMO in lubricant formulations. The goal was to determine whether the combined system of $Ti_3C_2T_x$ MXene, NDs, and GMO could significantly outperform both the base oil and single-additive systems (such as MXene only) in reducing friction and wear. A key achievement from this part of the study was to understand the mechanism of tribofilm formation, leading to improved frictional performance, and to fulfil the objective of achieving desirable tribological performance while paving the way for environmentally compliant formulation.

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2 Chapter 2: Material and Methods

2.1 Materials

GMO, serving as the organic friction modifier, primary ZDDP as the anti-wear additive, MoDTC as the inorganic friction modifier, and synthetic PAO oil (Synfluid PAO 6 cSt) as the base oil were supplied by TOTAL Energies, France. Carboxylated nanodiamonds (NDs) in two distinct forms were procured from Sigma Aldrich, UK:

- Type 1: Detonation nanodiamonds (DND) with an average diameter of 5 nm, dispersed in base oil at 0.1 wt% concentration.
- Type 2: Customised detonated nanodiamonds in dried form.

The rationale for purchasing NDs in two different media was that HRTEM characterisation of oil dispersed NDs was not feasible due to vacuum chamber constraints; therefore, dried NDs were required to verify particle size. Lubricant formulations were prepared by diluting nanoparticles and additives in the base oil. The dispersion process and concentration variations are detailed in each paper. In paper 1 and 2, the reported additive concentrations represent optimised values determined after varying ND concentrations (0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.3 wt%) and ZDDP concentrations (0.1 wt%, 0.2 wt%, and 1 wt%). As the supplier company could not confirm the dispersant used for carboxylated NDs, oleic acid was presumed to have been employed [1]. To validate this assumption, a lubricant containing oleic acid was also examined in Paper 1.

In paper 3 and 4, two different MXenes, $Mo_2TiC_2T_x$ and $Ti_3C_2T_x$ were utilised, both sourced from Nano plexus, UK. The selection criteria and characterization procedures for MXenes are discussed in detail in Papers 3 and 4. To ensure homogeneous dispersion of all additives, a magnetic stirrer was operated at 500 rpm for 1 hour. All experiments were conducted immediately after mixing to minimise sedimentation of additives within the lubricant.

2.2 Nanoparticle and Nanolubricant Characterisation

To determine the shape and size distribution of ND particles (type 2, in dried condition), $Mo_2TiC_2T_x$ and $Ti_3C_2T_x$ MXenes, an FEI Titan3 Themis 300 Scanning Transmission Electron Microscopy (STEM) instrument, which was equipped with Gatan Quantum ER energy filter was used.

Sedimentation experiments were conducted to assess the dispersibility and sedimentation behavior of NDs, $Mo_2TiC_2T_x$, and $Ti_3C_2T_x$ MXenes in the base oil. This method was selected as a practical approach for evaluating dispersion stability in nano lubricants, given that most conventional techniques require a dry medium [1]. Approximately 10 mL of each nano lubricant was transferred from the preparation beaker into transparent tubes, which were placed in a well-lit location for visual inspection. Dispersibility was monitored using photographic documentation at intervals of 1, 15, and 30 days [2] [3].

Viscosity measurements were performed using an Anton Paar Physica MCR301 rotational rheometer (UK). The viscosity of the nano lubricants remained comparable to that of pure PAO 6 base oil, even after additive incorporation, due to the low additive concentrations employed. Particle size analysis was conducted using a Malvern Zetasizer (UK) via Dynamic Light Scattering (DLS) for paper 1. Two lubricant formulations, PN0.05 wt% and PGZN0.05 wt%, were selected for measurement, with PN0.05 wt% serving as the reference lubricant. Other formulations exhibited higher agglomeration, making DLS measurements impractical, as discussed in paper 1.

2.3 Tribological Tests

Tribological tests were conducted using Cameron Plint TE 77 reciprocating tribometer, UK [4]. The pin used in the experiments applied the normal load on the contacting surface. Frictional force was measured by the force transducer, which was later used to calculate the average friction coefficient [5]. Material properties and dimensions of specimens are given in Table 2-1 and experimental conditions are given in Table 2-2. Maximum contact pressure was calculated using Hertzian contact theory. The tests were performed at 1 GPa contact pressure at 50 °C and 80 °C with a sliding speed of 0.2 m/s (5.0 mm stroke at 20 Hz) for 120 minutes. All the experiments were repeated three times to ensure repeatability under a boundary lubrication regime (Lambda ratio, $\lambda<1$) based on Hamrock-Dowson expression [6].

Table 2-1 Material properties of specimens.

Information	**Pin**	**Plate**
Material	**Steel EN31**	**Steel EN31**
Dimensions (mm)	**10 radius**	**7*7*3**
Hardness (HRC)	**58-62**	**58-62**
Roughness (nm)	**500**	**60-80**
Elastic modulus (GPa)	**190-210**	**190-210**

Table 2-2 Experimental conditions.

TE77 parameters	Value
Temperature ◦C	50,80
Contact pressure (GPa)	1
Load (N)	40
Frequency (Hz)	20

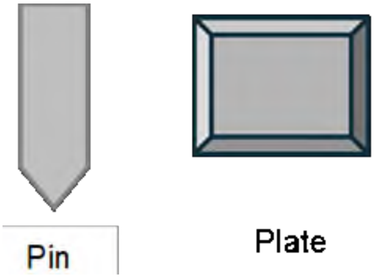

Figure 2-1 Schematic illustration of pin and plate.

In this work, the test temperatures were selected to simulate real engine conditions in conventional internal combustion vehicles and hybrid vehicles [7]. Before experiments, plates and pins were cleaned with heptane for 10 minutes in an ultrasonic bath and air dried. After the experiment, they were cleaned again in heptane to remove remaining oil fragments from the surfaces. Optical white light interferometry (WLI) was employed to measure volume loss on pin and plate surfaces following the tribological tests. Scanned images of pin surfaces were analysed using Vision64 software from Bruker Corporation. 3D image processing was performed to transform the curved surface into a flat area (to maximum flatness), carefully masking the worn area only. The software curve fitting tool (curvature and tilt) was used to transform the surface so that there was a worn contour in the middle of an undisturbed flat area. Then, the average radius of the wear scar (r), was determined from the worn area. The wear volume loss of the pin was later calculated by using the below equation:

$$V_{\text{pin volume loss}}=\frac{\pi h^2\,(3R-h)}{3} \quad \ldots\ldots(1)$$

$$h = R-((R^2-r^2))^{0.5} \quad \ldots\ldots(2)$$

Where, h = Spherical cap height (μm) R= Sphere radius (μm) r = wear scar radius (μm).

For the plate surfaces, the depths of the wear scars were very shallow, and in some cases, no measurable wear was detected by the white light interferometry. Hence, the roughness of the plate surfaces has been measured and reported. Surface roughness was measured by contact profilometer (Taylor Hobson 120L Talysurf), which employs a 2 µm conical-shaped diamond stylus drawn across the worn surface. Roughness values (Ra) were measured from three different places inside the wear track and averaged for the final Ra value. Later on, pin wear surfaces were also analyzed by an optical microscope (Leica Microscope, UK) [5].

2.4 Lubrication Regime Determination

The lubrication regime was determined by estimating the minimum film thickness and surface roughness. According to the Hamrock and Dowson equation[8], the Lambda ratio (λ) is used to determine the lubrication regime as written in, equation 3, which is represented by the ratio of minimum film thickness ($hmin$) to the composite surface roughness. Rq_1 and Rq_2 in equation 3 represent the root mean square surface roughness of interacting surfaces.

$$\lambda = \frac{h_{min}}{[{R_{q1}}^2+{R_{q2}}^2]^{\frac{1}{2}}} \qquad (3)$$

This study involves a pin-on-plate configuration, so the minimum film thickness is evaluated using equation 4.

$$\frac{h_{min}}{R'} = 3.63\left(\frac{U\eta_0}{E'R'}\right)^{0.68}(\alpha E')^{0.49}\left(\frac{W}{E'R'^2}\right)^{-0.073}(1-e^{-0.68k}) \qquad (4)$$

Where: E’ is the effective (reduced) Young’s modulus [Pa] (Equation 6); R’ is the reduced radius of curvature (Equation 5); W is the applied normal load [N]; α is the pressure–viscosity coefficient [Pa^{-1}]; k = 1 for circular contacts; η_0 is the dynamic viscosity of the oil at ambient temperature [Pa·s]; and U is the entrainment speed [m/s], defined as $U = (U_1 + U_2)/2$.

$$\frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2} \qquad (5)$$

$$E' = \frac{2E_1E_2}{(1-v_1^2)E_2+(1-v_2^2)E_1} \qquad (6)$$

where E_1, E_2 and v_1, v_2 are the Young’s moduli and Poisson’s ratios of the two contacting surfaces, respectively.

The maximum contact pressure is calculated in accordance with Stachowiak as given by Equation 7:

$$P_{max} = \frac{3W}{2\pi ab} \qquad (7)$$

where a and b are the contact zone dimensions [μm], determined from Hertz contact theory.

After putting the experimental conditions, the values for Lambda ratio are as below:

At 50°C: $\lambda \approx 0.026$

At 80 °C: $\lambda \approx 0.012$, showing that the experiments were run under boundary lubrication conditions.

The TE77 reciprocating tribometer operates with a sinusoidal velocity profile [9], which means that the lubrication regime must be assessed with particular care. Unlike unidirectional sliding contacts, for which the Hamrock–Dowson film thickness equations were originally developed, a reciprocating contact experiences a continuously changing sliding speed over each stroke. The speed falls to zero at the dead centres and reaches a maximum at mid stroke.

Under the operating conditions used in this study, the instantaneous velocity of the pin in the TE77 follows the relationship [10],

$v(t) = 2\pi f \cdot a \cdot \cos(2\pi f t)$,

where a represents the half stroke amplitude and f is the reciprocating frequency. This motion results in a mean sliding speed of 0.2 m/s, with the velocity dropping to zero at each reversal point.

Application of the Hamrock–Dowson equations require the mean entrainment speed u, defined as

$u = (u_1 + u_2) / 2$.

In the TE77 configuration, the plate remains stationary so u_2 equals zero, while the pin reciprocates with a mean sliding speed of 0.2 m/s, giving u_1 equal to 0.2 m/s. The resulting mean entrainment speed is therefore 0.1 m/s. This approach is widely accepted and considered appropriate for reciprocating contact conditions. Using this entrainment speed, the Hamrock–Dowson equation was applied together with the material properties, contact geometry, and lubricant viscosity relevant to the test system. The calculated lambda ratios at both test temperatures were well below unity, confirming that all experiments were conducted firmly within the boundary lubrication regime, in line with the descriptions provided in the experimental chapters.

It is important to understand that using a mean entrainment speed inevitably underestimates the severity of the contact conditions at the dead centres of each stroke. At these points, the instantaneous entrainment speed approaches zero and hydrodynamic film formation is no longer possible. As a result, full asperity to asperity contact occurs, and tribochemical reactions, tribofilm formation, and wear damage are most intense. This behavior is directly relevant to the tribofilm formation mechanisms examined throughout this thesis. Even at mid stroke, where the entrainment speed is highest, the lambda ratio remains well below unity, confirming that boundary lubrication persists throughout the entire reciprocating cycle.

2.5 Tribofilm Structural Analysis

To investigate the tribofilm structure, cross-sections were prepared with a high-resolution Focused Ion Beam (FIB, Helios G4 CX Dual Beam). For structural and compositional characterisation, the surfaces were transversely cut using FIB to fabricate cross-sectional lamellar specimens. Then prepared cross-sections were analysed with an FEI Titan3 Themis 300 Scanning Transmission Electron Microscopy (STEM) instrument equipped with Gatan Quantum ER energy filter, Energy Dispersive X-ray (EDX) and High-Angle Annular Dark-Field Scanning (HAADF).

With a high-performance cold field emission (CFE) SEM (Hitachi SU8230), the wear track on the plate surfaces was analysed after 120 minutes of tribological tests. The measurements were carried out at a beam voltage of 2.0kV and images were acquired at different magnifications. The measurements were carried out before and after using the EDTA solution on the wear track to remove the tribofilm by EDTA for understanding the surface wear mechanism [11]. Surface roughness was measured by a Taylor Hobson 120L Talysurf contact profilometer. Here, 2 μm conical-shaped diamond stylus was used for the measurement. Roughness values (Ra) were taken from three different places inside the wear track and averaged for the final Ra value.

A Dimension Icon Bruker AFM, USA, in a tapping mode was employed to image the surface morphology of the tribofilm. A silicon probe and a 125 μm long cantilever, comprising a lever force constant of 40 N/m and a resonant frequency of about 300 kHz were used. All the AFM images were obtained with a scan rate of 1 Hz over different selected areas in dimensions of 100 nm x 100 nm, 500 nm x 500 nm, 1 μm x 1 μm and 5 μm x 5 μm. Phase imaging mode was applied to perform the phase analysis with the same cantilever.

Static SIMS measurements were performed on the steel plates after the tribological tests using a Hiden Compact SIMS, equipped with a MAXIM-600P detector having a Hiden 6 mm triple quadrupole mass filter with facilities of pulse ion detection. The static SIMS has the following characteristics: Ar^+ primary ion with ion energy 5000V, emission 10.0 mA. The measured mass (m/Z) range was between 1-300. The sample area for positive and negative spectra is 800 x 800 $μm^2$. All the measurements were taken inside and outside of the wear track at two different locations to ensure reproducibility.

2.6 Overall Methodology: Justification of the Experimental Approach

The experiments were designed as a four-phase investigation, with each phase building directly on the insights gained from the previous one. Rather than exploring all possible additive combinations at once, a progressive strategy was deliberately adopted. This approach reflects that tribological behaviour in multi additive lubricant systems is highly sensitive to interactions between additives, many of which cannot be predicted from the behaviour of individual additives [12]. By increasing formulation complexity step by step, it was possible to clearly identify the role of each component, distinguish between synergistic and antagonistic effects, and use this understanding to guide the design of subsequent experiments.

All testing was carried out using a TE77 reciprocating pin on plate tribometer operating under boundary lubrication conditions at temperatures representative of those encountered in automotive engines. The TE77 was selected because its reciprocating motion closely mirrors the sliding conditions experienced by critical engine components such as piston rings and valve train contacts, where boundary lubrication dominates and tribofilm formation plays a central role in wear protection [13]. Steel on steel contacts were used throughout the study to maintain direct relevance to ferrous engine materials. Two test temperatures, 50 °C and 80 °C, were applied consistently across all phases to evaluate the temperature dependent activation of additive chemistry.

Analytical techniques were employed to characterise the tribofilms formed during testing. High resolution transmission electron microscopy combined with focused ion beam cross sectioning was used to directly observe tribofilm thickness and nanoparticle incorporation at the nanoscale level. Atomic force microscopy provided detailed maps of surface topography and adhesion, supplying nanoscale mechanical information. Static secondary ion mass spectrometry was used to obtain chemical fingerprints of the tribofilm surface, allowing additive derived elements to be detected. Raman spectroscopy was introduced in Phase 2 specifically to confirm the formation of MoS_2 from MoDTC tribochemistry, as its molecular level enables clear distinction between MoS_2 and other sulfur containing compounds. Across all phases, white light interferometry was used to measure wear volumes quantitatively, ensuring consistent and objective comparison of wear performance between formulations.

Phase 1 addressed a fundamental question: whether nanodiamonds could function effectively alongside glycerol monooleate and low concentrations of ZDDP to overcome the well documented friction wear trade off caused by GMO inhibiting ZDDP tribofilm growth. Nanodiamonds were selected because of their near spherical morphology, high hardness, and surface carboxyl groups, which made them promising candidates for reinforcing tribofilms.

In Phase 2, the formulation complexity was increased by introducing molybdenum dithiocarbamate, a widely used friction modifier in commercial engine oils. The key question was whether the interactions observed in Phase 1 would continue in commonly adopted additive environment. A full matrix of additive combinations was examined, displaying the performance of MoDTC, to the surrounding additive package. Raman spectroscopy played a crucial role in this phase by confirming MoS_2 formation, providing chemical evidence.

Phase 3 indicated a strategic shift away from further optimisation of conventional additive systems. Instead, $Mo_2TiC_2T_x$ MXene was introduced as a potential replacement for MoDTC, offering the prospect of molybdenum based friction reduction without the inclusion of sulfur or phosphorus [14]. A low concentration of ZDDP was maintained at this stage to operate as a benchmark, allowing the contribution of the MXene to be assessed before progressing to fully ZDDP free formulations.

Phase 4 integrated the mechanistic understanding developed across the earlier phases. In this final phase, $Ti_3C_2T_x$ MXene was combined with nanodiamonds and glycerol monooleate in a formulation containing no ZDDP or MoDTC. $Ti_3C_2T_x$ was chosen over $Mo_2TiC_2T_x$ because its behaviour in oil based systems is better documented, supporting interpretation of tribofilm chemistry [15]. ZDDP was included as a comparator to provide a direct reference against the conventional anti wear performance. Static SIMS was particularly valuable in this phase, as it enabled confirmation of tribofilm formation through tribochemical analysis even in the absence of traditional phosphorus and sulfur markers. The strong performance of this formulation validated not only the results of Phase 4, but also the overall experimental strategy and methodological logic underpinning the entire research plan.

2.7 References

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3 Chapter 3: Discussion

Chapter 3 provides a comprehensive discussion of the principal findings and outcomes presented in the appended papers. The pursuit of low-SAPS (sulfur, phosphorus, and ash) lubricants is driven by the dual objectives of achieving high-performance engine oils while reducing toxic emissions and complying with increasingly stringent environmental regulations. Conventional anti-wear additives such as zinc dialkyldithiophosphate (ZDDP) and friction modifiers like molybdenum dithiocarbamate (MoDTC) are widely recognised for their effectiveness; however, both contain sulfur and phosphorus (S/P), elements that contribute to harmful emissions and catalyst poisoning. Reducing their concentration in lubricant formulations without compromising wear resistance and friction performance remains a significant challenge.

This thesis addresses this challenge by investigating the synergistic interactions between nanoparticles and reduced concentrations of conventional additives to enable the development of environmentally friendly lubricants. The research adopts a systematic approach, beginning with formulations containing glycerol monooleate (GMO) and low concentrations of ZDDP, followed by the incorporation of nanodiamonds (NDs) as friction modifiers, and subsequently introducing novel two-dimensional (2D) materials MXenes to achieve advanced synergistic blends. This progressive methodology aims to maintain superior tribological performance while reducing the reliance on S/P-containing additives.

The results of this research are presented in paper 1–4, each contributing incrementally towards the formulation of eco-friendly nano-additive blends in polyalphaolefin (PAO) base oil. These blends are designed to form in-situ protective tribofilms under boundary lubrication conditions, thereby reducing friction and wear. Figure 3-1 illustrates the key considerations in developing P/S-free additive solutions, including additive selection, dispersion stability, tribofilm formation, and environmental impact. The following sections discuss the major findings in relation to the scope and objectives of the respective papers, highlighting the mechanisms underlying additive synergy, tribofilm characteristics, and performance under varying operating conditions.

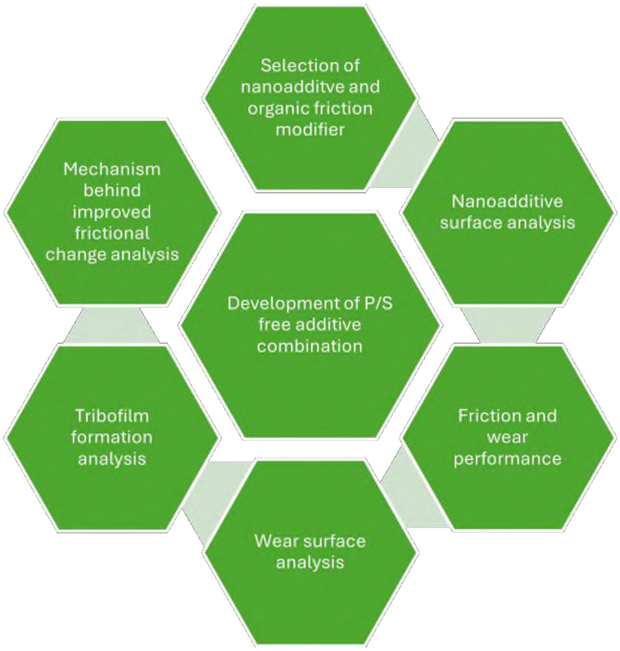

Figure 3-1 Illustration of the development of S/P free additive combination.

3.1 Hypothesis and Challenges

Paper 1 focused on investigating the synergistic effect between nanodiamond (ND) particles (~5 nm) and an organic friction modifier, glycerol monooleate (GMO), in a PAO base oil, with a low concentration of ZDDP included to mimic a low-SAPS formulation. The central hypothesis was that combining NDs with GMO would accelerate the formation of protective tribofilms and achieve lower friction compared to either additive used individually, while maintaining anti-wear protection with minimal levels of traditional high-S, high-P additives such as ZDDP. This addressed a critical scientific challenge: although GMO effectively reduces friction, it tends to inhibit the growth of ZDDP-derived anti-wear tribofilms, resulting in increased wear. By introducing NDs, the study aimed to overcome this friction–wear trade-off through tribochemical interactions that promote tribofilm formation without compromising wear resistance.

Building on the synergy observed between NDs and GMO, **paper 2** expanded the scope to a multi-additive system incorporating an inorganic friction modifier, molybdenum dithiocarbamate (MoDTC). MoDTC is widely used for friction reduction via tribochemical reactions that generate MoS_2; however, it introduces additional sulfur and typically requires ZDDP for anti-wear support. The objective of this study was to determine whether NDs could synergise with both GMO and MoDTC simultaneously. Specifically, the research evaluated whether NDs could become entrained within the MoDTC-derived MoS_2 tribofilm, thereby enhancing friction and wear performance. The key hypothesis was that a multi-additive system comprising ND + GMO + MoDTC + low-ZDDP would deliver the lowest friction, whereas partial combinations (e.g., ND + MoDTC without GMO or ZDDP) might exhibit reduced effectiveness or even antagonistic behaviour. This investigation was motivated by the broader goal of developing low-SAPS lubricants. If NDs could sufficiently reduce friction, it might be possible to significantly reduce or eliminate MoDTC and ZDDP content in future formulations. However, understanding the interaction between NDs and MoDTC was essential, given the limited and inconsistent findings in prior literature regarding nanoparticle–MoDTC synergy.

To further explore additive synergy, **paper 3** introduced a different class of nanostructured material, MXenes into lubricant formulations. MXenes, a family of two-dimensional transition metal carbides, were selected due to their exceptional mechanical and tribological properties. In particular, $Mo_2TiC_2T_x$ MXene, a two-transition-metal carbide containing molybdenum, was investigated for its potential to reduce friction and wear when combined with a small concentration of ZDDP and GMO. The hypothesis was that $Mo_2TiC_2T_x$, owing to its unique lamellar structure and lubricious Mo content, could form a tribofilm that protects surfaces under boundary lubrication, even with ~0.2 wt% ZDDP. Previous studies had shown that $Ti_3C_2T_x$ MXene (which lacks Mo) provides promising friction reduction due to facile interlayer shear; therefore, incorporating Mo into the lattice was expected to enhance friction and wear performance, as Mo is known to promote low friction through mechanisms such as MoS_2 formation. Unlike MoDTC, $Mo_2TiC_2T_x$ MXene contains no P or S elements, offering a potential pathway to Mo-based friction reduction without introducing harmful S/P compounds. The overarching goal of Paper 3 was to demonstrate a sustainable friction modifier combination $Mo_2TiC_2T_x$ + GMO + low-ZDDP, that achieves high tribological performance while reducing ZDDP dependency. However, the results indicated that this formulation did not outperform the ND-based system developed in Paper 1, highlighting the complexity of achieving optimal synergy among additives.

Paper 4 focused on developing a fully phosphorus- and sulfur-free additive combination by eliminating ZDDP and relying exclusively on a pair of nanomaterials in conjunction with an organic friction modifier. This study investigated $Ti_3C_2T_x$ MXene, a two-dimensional transition metal carbide combined with nanodiamonds (NDs) and GMO to determine whether their synergy could form protective tribofilms under boundary lubrication conditions. The overarching goal was to achieve excellent friction and wear performance using only “green” additives, thereby demonstrating the feasibility of a completely P- and S-free nano-additive formulation.

The central hypothesis was that $Ti_3C_2T_x$ MXene could act as a solid lubricant and potentially participate in tribofilm formation due to its layered structure and high shear capability. By combining $Ti_3C_2T_x$ MXene with NDs and GMO, both of which had shown promising results in **paper 1**, the expectation was to create a three component synergy capable of delivering low friction and minimal wear without relying on conventional additives such as ZDDP or MoDTC. Fundamentally, this study examined whether the ND + $Ti_3C_2T_x$ MXene + GMO blend could fully substitute for ZDDP/MoDTC while still providing robust surface protection.

The primary objectives were twofold:

- 1.To evaluate whether the $Ti_3C_2T_x$ MXene + ND + GMO formulation outperforms the base oil and single-additive systems (e.g., MXene-only, ND-only) in terms of friction reduction and wear resistance.
- 2.To characterise the tribofilm formed by these additives using advanced surface analysis techniques, thereby elucidating the mechanisms responsible for their tribological behaviour.

This study represents a critical step toward sustainable lubrication strategies by demonstrating the potential of P/S-free additive systems. However, the findings also highlight the complexity of achieving complete functional replacement of traditional additives, underscoring the need for further optimisation and mechanistic understanding.

3.2 Tribological performance

Paper 1 investigates the synergistic effect on friction and tribofilm formation by ND-GMO formulation. This part of the research showed that at 50 °C, adding 0.05 wt% ND to GMO (PGN0.05) reduced the steady-state COF to ~0.06, which was the lowest among all lubricants at that temperature. This was considerably below the COF of ~0.08 for ND alone (PN0.05) and ~0.09 for GMO alone. At 80 °C, the three additive combinations (GMO+ZDDP+ND, denoted PGZN0.05) achieved an even superior friction reduction: after ~40 min run-in, COF dropped to ~0.04. Showing the lowest friction of any formulation tested. This lubricant formula indicated that NDs can maintain ultra-low friction at elevated temperature when combined with GMO and a low concentration of ZDDP. In parallel with friction reduction, wear performance was improved or sustained by ND inclusion. At 80 °C, all ND-containing lubricants revealed reduced or similar wear against their ND-free counterparts. The ZDDP+ND oil (PZN0.05) lubricant formulation attained the lowest wear volume among all tested lubricants at 80 °C. However, the lubricant GMO+ZDDP+ND (PGZN0.05) showed comparable wear volume loss at that temperature.

With the developed synergy between ND and GMO, **paper 2** expanded the scope to a multi-additive system, including an inorganic friction modifier, MoDTC (molybdenum dithiocarbamate). The frictional tests of these multi-additive system confirmed that NDs can both act synergistically and antagonistically depending on the presence of supporting additives. The lowest friction coefficients were achieved when all four additives were combined (formulation *PMoGZN*: MoDTC + GMO + ZDDP + ND) at both test temperatures. PMoGZN exhibited a steady COF which clearly outlined friction reduction, demonstrating the synergy among all additives. At 80 °C, lubricants with NDs and all other additives showed COF values on the order of ~0.05 (close to paper 1's best case), whereas MoDTC alone or MoDTC+GMO gave higher friction, ~0.08–0.1 (comparable to baseline GMO+ZDDP). The advantage of using NDs was evident by comparing PMoGZ vs. PMoGZN. It showed that adding NDs to the MoDTC+GMO+ZDDP lubricant lowered COF by around 10–20% and stabilised friction over time. Conversely, when certain additives were absent, NDs did not reduce friction, as indicated by the frictional results. The lubricant formulation PMoN (MoDTC + ND without GMO or ZDDP) showed an antagonistic effect at both temperatures, its friction was higher than MoDTC alone. This indicates that if NDs are not adequately adhered to the tribofilm, free NDs can increase friction (likely through abrasion or by disrupting the MoS_2 layer). A similar observation was seen for lubricant PMoGN (MoDTC + GMO + ND, no ZDDP). While GMO could help with friction reduction, the absence of ZDDP's robust film meant NDs were partially entrapped, yielding inconsistent friction with higher wear. These outcomes emphasised that NDs require a complementary tribofilm that will act as a matrix (either a ZDDP phosphate or a well-formed MoS_2 tribofilm) to achieve the friction and wear reduction goal. In presence of such matrix, as seen in PMoGZN, NDs significantly improved friction, however, when it is inadequate, NDs could become a liability. From wear surface analysis, the formulation PMoGZN did not show best wear reduction performance as it showed in the frictional tests. Except for PMoZN, NDs did not contribute to reduce wear. The presence of GMO molecules and NDs could have interrupted the formation of phosphate and MoS_2 films. The surface observation illustrates abrasive wear, likely attributable to the presence of nanodiamonds with superior hardness, potentially resulting from inadequate dispersion, which caused surface scratching or damage.

Paper 3 investigates the effectiveness of $Mo_2TiC_2T_x$ MXenes as a lubricant additive. From the tribological results, it is evident that success of $Mo_2TiC_2T_x$ MXenes as an additive highly depends on the additive combination and operating temperature. At elevated temperature, the frictional performance of the lubricant containing $Mo_2TiC_2T_x$ (PMox) provided marginal improvement compared to base PAO oil [1]. However, at both temperatures, the wear performance also showed that PMox nanolubricant did not improve wear properties; rather, an abrasive effect was observed from the wear surface analysis. When $Mo_2TiC_2T_x$ MXenes were incorporated with GMO (formulation PGMox), a noticeable reduction in friction was observed at both 50 °C and 80 °C, when compared with the frictional performance of PMox nanolubricant. One of the prominent reason could be affinity of GMO to get adsorbed onto steel surface developing a lubricating tribofilm [2]. This tribofilm further facilitated the reduction in wear volume loss on the pin surface. When ZDDP was combined with $Mo_2TiC_2T_x$ (PZMox), the friction reduced slightly in comparison with PMox nanolubricant. However, the frictional performance of PZMox was not as significant as that of PGMox and PGZMox nanolubricant. ZDDP itself is an anti-wear additive and is well-known to form thick patchy tribofilm. This tribofilm, rather than reducing friction, increases it due to its higher roughness [3]. The formulation containing GMO, ZDDP and $Mo_2TiC_2T_x$ MXenes (PGZMox) exhibited the most significant improvements in both friction and wear behaviour at 80 °C. PGZMox exhibited the lowest COF and wear volume loss, indicating the presence of synergy among additives in the lubricant formulation under severe conditions. However, the tribological performance was not up to the range, attained in paper 1.

Paper 4 explores the effectivity of $Ti_3C_2T_x$ MXenes along with NDs and GMO as lubricant additive. Remarkably, without any traditional additive, the $Ti_3C_2T_x$ + ND + GMO blend achieved substantial reductions in friction and wear. By comparing the frictional results, it was determined that the three additive formulations outperformed not only the base oil but also any two-additive combinations. For example, $Ti_3C_2T_x$ MXenes alone did reduce friction to some extent, but its wear protection was limited. ND+GMO (from paper 1) provided low friction but needed ZDDP for better wear protection. In this research, a synergistic effect was evident, when all three additives were combined, especially at higher temperature. The friction coefficient dropped significantly and stabilised at a low value. Similar to friction, wear scars were minimal. The PGNMx nanolubricant could substantially reduce friction and wear compared to the base oil and the lubricant containing only MXenes. Quantitatively, at 80 °C for PGNMx steady COF of around ~0.04 (like paper 1) was achieved, whereas MXenes-only lubricant has higher COF ~0.07–0.08 and base oil around 0.11–0.12. Wear volume loss and surface analysis showed that the lubricant containing three additives yielded the smallest wear scars and smoothest tracks, while single additives did not yield better protection. These outcomes endorse that ND and GMO noticeably enhance the lubricity with $Ti_3C_2T_x$ MXenes, enabling it to perform as a potential substitute for ZDDP/MoDTC in protecting steel contacts.

3.3 Tribofilm chemical and physical properties

An interesting finding in **paper 1**, not reported before, was direct evidence that NDs form a tribofilm as well as integrate into the tribofilm. Cross-sectional FIB-TEM analysis showed that the ZDDP+GMO oil (PGZ) formed a very thin phosphate film (~3–5 nm after 2 h) on the steel surface. In contrast, the ND-containing lubricant (PGZN0.05) developed a thicker tribofilm with a thickness of around 20–22 nm on the steel surface (Figure 3-2) and this tribofilm further reduced friction as well as wear. The TEM images revealed spherical ND particles embedded throughout the tribofilm. These images confirmed the presence of several ~5 nm carbonaceous spheres (consistent with ND size) dispersed within the tribofilm.

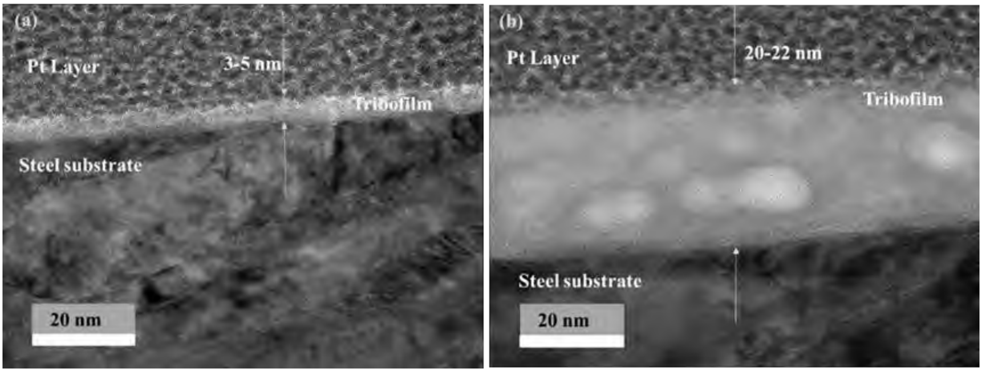

Figure 3-2 HRTEM images for formed tribofilm at 80 °C for (a) PGZ and (b) PGZN0.05 wt% [1].

EDX elemental analysis further indicated that these spherical inclusions were carbon-rich (identified as NDs), while the surrounding segment of the tribofilm contained Zn, P, S, and O from ZDDP chemistry. This indicates NDs were successfully entrained and retained in the protective tribofilm.

From this analysis, a synergistic mechanism for improved tribological performance was proposed: during sliding, GMO molecules adsorb on the steel surface due to their affinity towards the steel surface and on ND surfaces (NDs were already modified with surface carboxyl groups, which can chemically bind with GMO's polar head). This led to a tribochemical interaction, resulting in the "encapsulation" of NDs by organic layers. Under high contact pressure, NDs readily penetrate between asperities contacts (their ~5 nm size is expected to be below the asperity scale) and cause them to develop rolling or sliding motion, producing a micro-polishing effect that smooths the surfaces. The rolling motion of the NDs can reduce friction by shifting some sliding to microscale rolling contact and by lessening asperity sharpness due to their hardness. Notably, the NDs also promote faster tribofilm growth. The hypothesised mechanism is shown schematically in Figure 3-3 below.

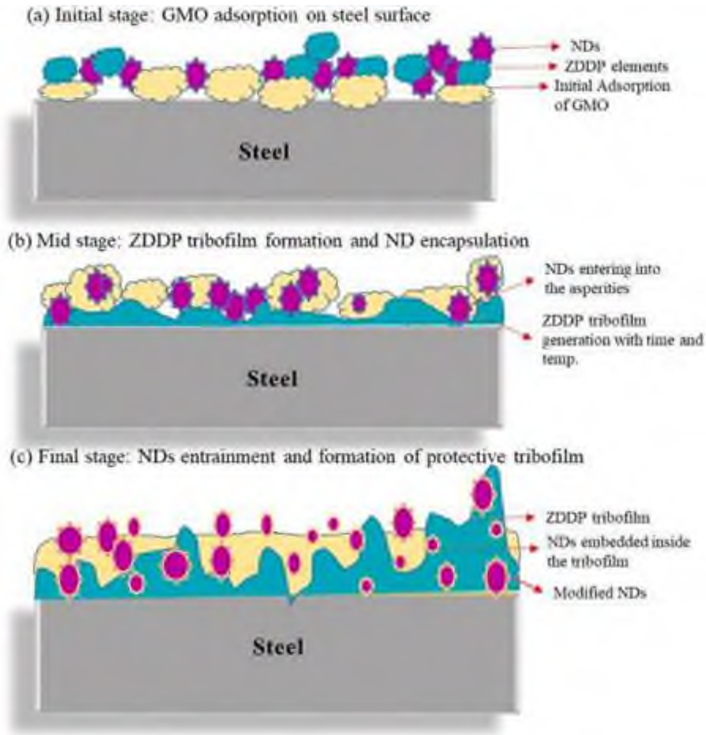

Figure 3-3 Schematic illustration of friction reduction mechanism [1].

With temperature and time, ZDDP molecules activate and develop phosphate-rich tribofilm. Once the phosphate tribofilm starts to form, NDs become mechanically interlocked inside the tribofilm. This interlocking prevents the nanodiamonds from causing three-body abrasion and reinforces the load-bearing capacity of the film. In summary, GMO's adsorption provided initial friction reduction properties and chemical affinity towards NDs, and NDs' presence led to a thicker, less adhesive tribofilm where decomposed ZDDP tribofilm acted as a matrix for these NDs to be mechanically interlocked and provide better wear protection. Paper 1 thus achieved its goal by demonstrating a novel ND+GMO+ZDDP (PGZN0.05) lubricant that delivered significantly reduced friction (~0.04) and reduced wear at a low ZDDP concentration. This study provided the first direct validation of NDs embedment in a tribofilm and confirmed that eco-friendly carbonaceous nanoparticles can synergistically improve tribological performance.

In paper 2, the formation of tribofilms from lubricant formulations such as PMoGZN was examined using SEM, AFM, and TEM analyses, revealing the embedment of NDs within the tribofilm. The smoothest surface topography, mechanically achieved with these formulations, evidences that NDs imparted a polishing effect, responsible for surface roughness reduction and friction reduction. The explanation for this effect lies in the spherical shape of the NDs, which allows them to fill surface asperities and thus form a resistant tribofilm. The term “mechanical interlocking” describes the embedding of NDs into the tribofilm, where they serve as reinforcing agents to enhance tribofilm stability. If integrated properly, such NDs prevent wear by maintaining the integrity of the tribofilm underload and reducing friction. However, in non-embedded situations, NDs behave like abrasive particles, roughening the surface and resulting in higher friction and wear in some of these formulations.

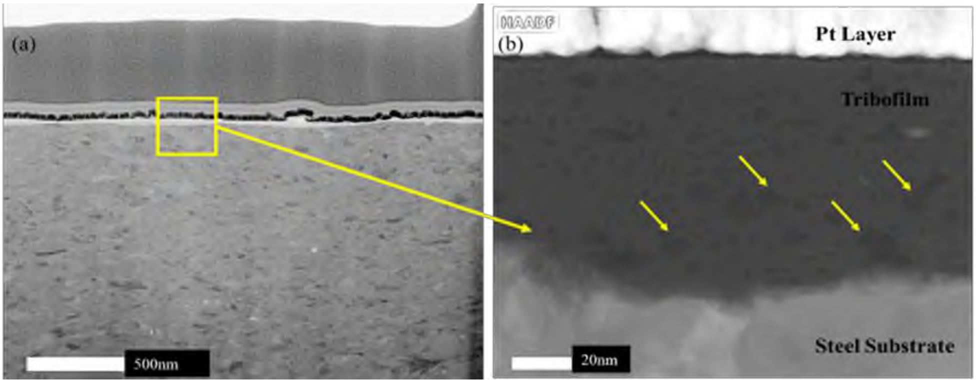

Figure 3-4 HRTEM images of tribofilm formed on steel surface, showing (a) cross-section of tribofilm for PMoGZN lubricant, (b) HAADF image for cross-section of tribofilm.

Consequently, the movement of nanoparticles is predominantly governed by the overall behavior of the oil in bulk. GMO also plays a critical role by forming a low-shear boundary layer that further enhances tribological performance when combined with MoDTC, ZDDP and NDs. The anti-wear tribofilm of ZDDP and the friction-reducing properties of GMO resulted in a synergistic effect that is dominant in the PMoGZ system. The synergistic effect with nanoparticles preferentially occurred in the PMoGZ system, as NDs were better integrated into the tribofilm. The ZDDP-derived phosphate layer provided a stable matrix for the ND embedment, as seen in the HRTEM analysis in Figure 3-4, which improved the tribological performance. While incorporating NDs also improved the PMoG system, the absence of ZDDP might have reduced the robustness of tribofilm, limiting the synergy. Further, the friction reduction performance was facilitated by the formation of MoS_2 by the tribochemical reaction of MoDTC. The inclusion of NDs and GMO did not interrupt friction reduction; rather, a synergistic effect was found between MoDTC and

NDs that further improved the tribological performance of the newly developed nanolubricant PMoGZN.

In **paper 3**, the surface analysis revealed that effectiveness of $Mo_2TiC_2T_x$ MXenes as lubricant additive highly depends on the additive combinations. Figure 3-5 shows the SEM images of the plate wear scars following 2 hours of testing at 80 °C. The wear scar from the PMox (Figure 3-5 (a)) exhibits significant surface degradation and distinct abrasive grooves.

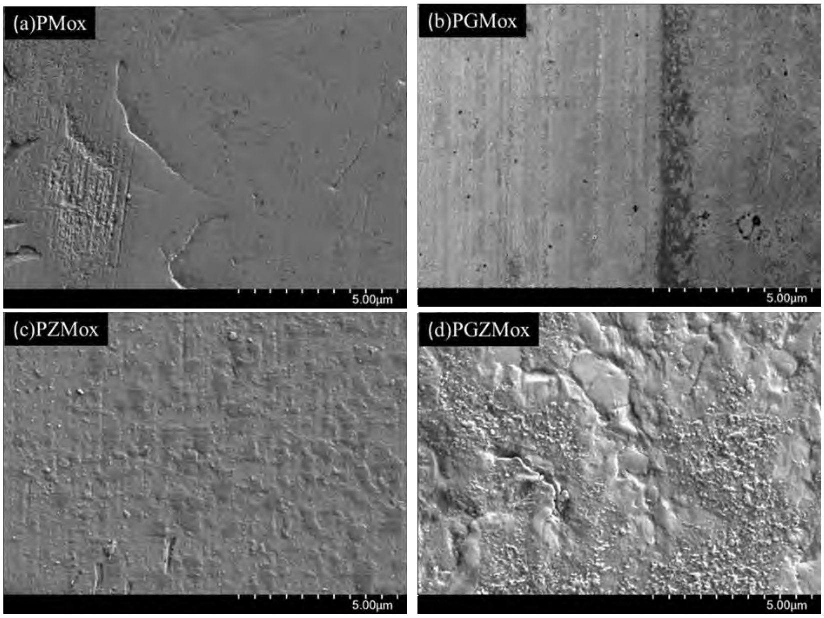

Figure 3-5 SEM images of the wear scar of plate surfaces for lubricants tested at 80 °C.

In contrast, the plate surfaces lubricated with PGMox and PZMox showed less surface damage compared to the PMox lubricated plate (Figure 3-5 (b)). This could be due to the formation of a tribofilm that reduces direct metal-to-metal contact and helps MXene nanoflakes slide rather than abrade [4]. Similarly, from Figure 3-5 (c), it can be observed that the PZMox lubricated plate surface is much smoother and covered with a patchy tribofilm-like layer instead of cutting grooves. This patchy surface resembles the typical structure reported for ZDDP tribofilms [1]. As a result, the PZMox showed only mild wear features and less pronounced grooves compared to the PMox. Figure 3-5 (d) shows the wear surface of the plate for PGZMox lubricant. From the SEM image, it appears that a continuous film covers the wear surface, protecting it from further wear. The SEM and optical analyses revealed abrasive wear, suggesting that without surface active agents, $Mo_2TiC_2T_x$ MXene alone does not improve friction and wear, but rather acts as loose third-body abrasives rather than an effective lubricant additive. According to the experimental and post experimental analysis, the formulation containing GMO, ZDDP and $Mo_2TiC_2T_x$ MXenes (PGZMox) exhibited the most significant improvements in both friction and wear behaviour at 80 °C. PGZMox exhibited the lowest COF and wear volume loss, indicating synergy among the additives in the lubricant formulation under severe conditions.

In **paper 4**, the most prominent evidence of synergy was formation of a thick tribofilm of approximately 150 nm in thickness on the steel surface when using the PGNMx nanolubricant. Cross-sectional TEM imaging revealed a thick tribofilm covering the wear track in the triple-additive system and shown in Figure 3-6.

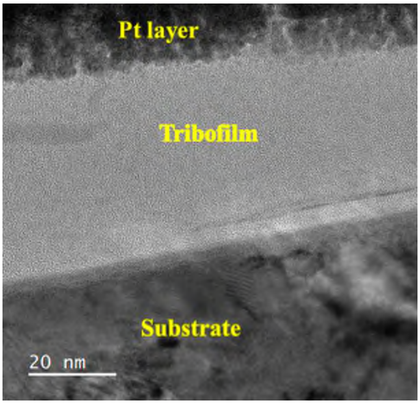

Figure 3-6 HRTEM images of the PGNMx tribofilm formed at 80 °C.

This PGNMx tribofilm was noted to be robust, without the patchy structure typical of ZDDP films. Its composition, analysed by SIMS, indicated predominantly C, O, Ti, and Fe (consistent with a mix of a carbonaceous matrix, TiOx from MXene, and iron oxide at the interface). The tribofilm formation mechanism proposed involves few steps: (1) Adsorbance of GMO molecules (GMO can decompose at ~80 °C to form bonded organic layers). (2) MXene nanosheets entering into the asperity contact and by the rubbing action are mechanically sheared and exfoliated into thinner layers. These nanosheets might spread out and align parallel to the surface, (3) NDs flow around and polish the interface, helping to compress and combine the MXene layers into a thick film. Through this concentrated action, a thick film builds up in situ, consisting of MXene platelets (providing easy shear), carbon/organic phases derived from ND surface carbon and decomposed GMO that provides ductility and adherence, and possibly some iron oxide from tribo-oxidation which can help bond layers to the steel. This nanoadditive combination can effectively decrease or replaces the traditional ZDDP rich lubricant that prevents metal-to-metal contact, thus suppressing wear, thus reducing friction.

The performance of this P- and S-free tribofilm was notable, the PGNMx lubricant achieved better tribological performance without any ZDDP, reaching nearly the same tribological performance previously only seen with ZDDP-containing formulations. Paper 4 summarises that this additive formulation (PAO + GMO + ND + $Ti_3C_2T_x$) is a promising path toward P- and S-free additive combination, in line with environmental demands for greener tribological solutions, since it provides lower friction and wear without compromising the protection level of contacting surfaces.

3.4 Progression and Links Between Phases

The four experimental phases of this thesis describe a clear and logical progression from conventional low-SAPS lubricant formulations toward a fully phosphorus and sulfur free additive system. Each phase increased formulation complexity in a careful and controlled way, building directly on the mechanistic understanding developed in the previous stage. Together, the phases show how friction and wear reduction mechanisms evolved as new additives were introduced and how the insights gained at each step informed the overall research direction.

In Phase 1, the foundational synergy of the research programme was established using nanodiamonds, glycerol monooleate, and a low concentration of ZDDP. The optimised formulation delivered a low coefficient of friction and a substantial reduction in wear at elevated temperature compared with the base oil. This performance was achieved through a combination of processes, including GMO adsorption on the steel surface, tribochemical encapsulation of nanodiamonds, and the formation of a phosphate rich tribofilm from ZDDP. The nanodiamonds became embedded within this tribofilm, increasing its thickness and contributing to surface polishing. Importantly, this phase provided direct experimental evidence of nanodiamonds incorporated within a tribofilm, confirming a mechanism that had previously only been proposed in the literature. However, ZDDP remained essential as the structural matrix, limiting the environmental performance of the formulation.

Phase 2 examined whether this nanodiamond synergy could be maintained in a more complex and commercially relevant additive environment that included molybdenum dithiocarbamate. The optimised formulation achieved the lowest friction values in this phase, showing that nanodiamond synergy was preserved and even enhanced when MoDTC was present. The tribofilm now combined MoS_2 formed from MoDTC with phosphate elements from ZDDP, within which nanodiamonds were embedded and mechanically reinforced the film. GMO again played a key role by ensuring effective integration of nanodiamonds into the tribofilm. This phase also revealed a critical limitation, as nanodiamonds combined with MoDTC alone disrupted tribofilm formation and increased wear. This finding demonstrated that nanodiamond performance depends strongly on the surrounding additive environment and reinforced the importance of formulation design.

Phase 3 marked a strategic shift toward the use of two-dimensional nanomaterials, introducing $Mo_2TiC_2T_x$ MXene as a potential alternative to sulfur containing friction modifiers. In this phase, friction and wear reduction were governed mainly by the lamellar shear behaviour of MXene nanoflakes and their interaction with GMO and ZDDP at the sliding interface. The MXene provided solid lubrication through easy interlayer shear, while ZDDP stabilised the tribofilm and prevented direct metal contact. When used without supportive additives, MXene acted as an abrasive, reinforcing the conclusion that nanomaterials require a suitable additive framework. However, as the required level of friction and wear was not achieved in comparison with the phase 1, the motivation shifted towards the widely used titanium based Mxenes due to their extensive mechanical and tribological properties. Building on this understanding, Phase 4 combined $Ti_3C_2T_x$ MXene, nanodiamonds, and GMO in a formulation without ZDDP or MoDTC. This final phase delivered the best overall tribological performance through the combined action of boundary film formation, solid lubrication, and mechanical interlocking, demonstrating that a robust and protective tribofilm can be achieved without phosphorus or sulfur containing additives.

This is a critical confirmation of the thesis objective. It shows that $Ti_3C_2T_x$ MXene can be synthesized in bulk as they are scalable nanomaterials and NDs are commercially available in large quantities. Hence, both can be combined to create a "novel" tribological solution with GMO to meet performance requirements without relying on additives that produce sulfuric or phosphoric emissions.

3.5 Reference

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4 Chapter 4: Limitations, Future Work and Conclusion

4.1 Limitations of the Present Study

The primary technical limitation of this study arises from the complex physicochemical behaviour of nano-additives within lubricant formulations. Achieving a uniform and stable dispersion of nanolubricants containing nanodiamonds (NDs) and MXene flakes in the base oil proved to be a significant challenge. Commercially produced nanoparticles, including NDs, often exhibit broad particle size distributions, irregular morphologies, and surface impurities. These characteristics promote strong interparticle interactions, leading to rapid agglomeration and sedimentation unless extensive surface modification techniques are employed. Such instability compromises the homogeneity of the lubricant and reduces the effective concentration of active particles at the tribological interface, which is critical for tribofilm formation.

Similarly, MXenes such as $Ti_3C_2T_x$ and $Mo_2TiC_2T_x$ possess surface termination groups (–OH, –O, –F) that impart hydrophilic properties, severely limiting their dispersibility in non-polar lubricants such as PAO-based oils. Previous research by Feng et al. [1], reported that MXenes tend to cluster or stack when dispersed in pure oil, with only marginal improvements observed when unmodified $Ti_3C_2T_x$ was introduced into castor oil. Consistent with these findings, the present study observed that dispersion stability was particularly critical when MXenes were combined with other additives without prior surface functionalisation. The absence of chemical modification or surfactant-assisted dispersion likely exacerbated particle clustering, reducing the uniformity of additive distribution and potentially delaying the formation of a continuous tribofilm.

In addition to dispersion-related challenges, nanoparticle availability and production constraints further limit the scalability of this work. The NDs and MXenes employed in this study were laboratory-grade materials, whereas industrial powders often exhibit batch-to-batch variability in particle size, morphology, and surface chemistry. Such inconsistencies can significantly influence lubricant behaviour and tribological performance. Furthermore, MXene synthesis typically involves hazardous chemicals such as hydrofluoric acid (HF), raising concerns regarding safety, environmental impact, and scalability. Producing these nano-additives at ton-scale quantities while maintaining consistent quality remains technically demanding and economically costly. Nevertheless, emerging research on alternative synthesis routes for MXenes and NDs offers promising opportunities to produce these materials more safely and sustainably, thereby facilitating their integration into large-scale lubricant formulations.

In summary, while this research demonstrates the potential of MXenes and NDs to enhance tribological performance through synergistic tribofilm formation, several limitations including nanoparticle scale-up barriers, dispersion instability, and restricted test conditions, highlight the gap between laboratory findings and real-world applications. Addressing these challenges through advanced dispersion techniques, scalable synthesis methods, and extended tribological testing will be essential to fully realise the benefits of these nano-additives and advance the development of environmentally friendly, high-performance lubricants.

4.2 Future Perspectives:

To advance the findings of this study and overcome the identified limitations, future research should focus on the following areas. In particular, further work is required to translate the promising laboratory-scale tribological performance of MXene-based and nanodiamond-based additive systems into robust, application-ready lubricant formulations. Greater emphasis should be placed on understanding long-term stability, additive–additive interactions, and performance under realistic operating conditions, including varying loads, temperatures, and sliding regimes. Addressing these challenges will be essential for bridging the gap between fundamental tribochemistry and practical deployment in next-generation, environmentally compliant lubrication systems.

1. Chemical Functionalisation and Advanced Dispersion Techniques

Achieving uniform and stable dispersion of nano-additives remains a critical challenge. Future work should explore chemical functionalisation strategies to improve compatibility between hydrophilic MXenes and non-polar lubricant matrices. Techniques such as high-shear mixing, high-power ultrasonication, and the incorporation of surface-active surfactants can significantly enhance dispersion stability. Previous studies have demonstrated improved dispersion for nanodiamonds (NDs) through such methods; therefore, similar optimisation for MXenes could enable the development of nanolubricants with uniformly dispersed nanoparticles. This would facilitate consistent tribofilm formation and improve overall tribological performance.

2. In-Situ Tribofilm Monitoring

Real-time monitoring of tribofilm formation is essential for understanding the mechanisms that govern friction and wear reduction. Advanced in-situ analytical techniques, such as Raman or infrared spectroscopy, can provide chemical insights into tribofilm growth during sliding. Additionally, quartz crystal microbalance (QCM) methods can track nanoscale mass changes, enabling correlation between tribofilm development and frictional behaviour. Deploying these techniques will allow researchers to establish direct relationships between additive chemistry, tribofilm evolution, and tribological performance under dynamic conditions.

3. Exploration of Biodegradable Base Fluids

To fully realise the concept of “green” lubrication, future studies should investigate biodegradable base oils as carriers for nano-additives. MXenes, due to their hydrophilic nature, are expected to disperse more effectively in polar lubricants such as ionic liquids, vegetable-oil esters, glycols, and glycerol. Systematic trials are required to identify formulations that maintain low friction and wear while minimising environmental toxicity. This approach aligns with sustainability goals and could significantly reduce the ecological footprint of lubricant systems.

4. Life-Cycle Environmental Assessment (LCA)

To ensure the sustainability of nano-additive-based lubricants, comprehensive life-cycle assessments should be conducted. These assessments must quantify energy consumption, emissions, and potential toxicity associated with nanomaterial production, use, and disposal. Given that MXene synthesis often involves hazardous reagents and energy-intensive processes, LCA frameworks will help determine whether the tribological benefits outweigh the environmental and economic costs. Incorporating sustainability metrics early in the development process will guide the design of truly low-impact, high-performance lubricants. Opportunities such as recycling worn additives and integrating renewable energy into manufacturing should also be explored.

4.3 Reference

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4.4 Summary and Conclusion

A clear evolutionary path is seen across these four studies, toward an environmentally friendly nanoadditive combination, capable of forming tribofilms in situ under boundary lubrication. The primary aim of this study was to explore and exploit the synergies between low concentrations of nanoparticles and conventional lubricant additives as a novel approach for developing low-SAPS lubricants. A multi-additive, mechanism-led research approach has been used in this work by combining GMO, nanodiamond and MXene to develop robust tribofilm that performed better than any single additive system. The tribological performance then linked with extensive surface analysis techniques to see exactly which combination performed better and to understand the friction and wear reduction mechanism. From there, a clear substitution pathway was established, starting with reduced ZDDP concentrations and progressing to ZDDP-free formulations, while maintaining minimal friction and wear. The key conclusions from the publications are stated below.

- **Paper 1 (ND + GMO + Low ZDDP in PAO):**
  - Low concentration of carboxylated nanodiamonds (0.05 wt%) significantly increased tribofilm thickness (3–5 nm → 20–22 nm), reducing friction by ~60% and wear by ~45% at 80 °C.
  - Synergistic interaction between GMO and NDs enabled adsorption, controlled decomposition, and mechanical interlocking within ZDDP tribofilm, enhancing tribological performance.
  - Demonstrates potential for low-SAPS lubricants using ND/GMO synergy with minimal ZDDP.
- **Paper 2 (NDs with MoDTC, GMO, ZDDP):**
  - Proper embedment of NDs within tribofilm prevents abrasive behaviour and stabilises sliding surfaces.
  - Formulation PMoGZN (MoDTC + GMO + ZDDP + NDs) achieved lowest friction at 50 °C and 80 °C, confirming additive synergy.
  - Highlights that ND performance depends on tribofilm integration, paving the way for reduced P and S content in lubricants.
- **Paper 3 ($Mo_2TiC_2T_x$ MXene with GMO + ZDDP):**
  - $Mo_2TiC_2T_x$ MXene alone showed no friction/wear benefit; acted as abrasive particles.
  - Addition of GMO and low ZDDP enabled temperature-activated synergism, forming a robust tribofilm and improving tribological behaviour.
  - Demonstrates $Mo_2TiC_2T_x$ MXene's role as a partial ZDDP replacement, supporting eco-friendly lubricant development.
- **Paper 4 ($Ti_3C_2T_x$ MXene + GMO + NDs):**

- $PGNM_x$ formulation (PAO + GMO + NDs + $Ti_3C_2T_x$) achieved the greatest reduction in friction and wear, outperforming ZDDP-based blends.
- Synergy among GMO, NDs, and MXene promoted formation of a thicker, lubricious tribofilm, offering a P- and S-free solution aligned with sustainability goals.

All studies confirm that synergistic interactions among organic friction modifiers (GMO), nanodiamonds, and MXenes are critical for tribofilm formation and tribological performance. These findings collectively pave the way for the development of eco-friendly, high-performance lubricants that minimise reliance on phosphorus- and sulfur-based additives, reducing environmental impact while improving energy efficiency.

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