

A review of current understanding in tribochemical reactions involving lubricant additives

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Abstract: Lubricants have played important roles in friction and wear reduction and increasing efficiency of mechanical systems. To optimize tribological performance, chemical reactions between a lubricant and a substrate must be designed strategically. Tribochemical reactions are chemical reactions enabled or accelerated by mechanical stimuli. Tribochemically activated lubricant additives play important roles in these reactions. In this review, current understanding in mechanisms of chemical reactions under shear has been discussed. Additives such as oil-soluble organics, ionic liquids (ILs), and nanoparticles (NPs) were analyzed in relation to the tribochemical reaction routes with elements in metallic substrates. The results indicated that phosphorus, sulfur, fluorine, and nitrogen are key elements for tribochemical reactions. The resulting tribofilms from zinc dithiophosphates (ZDDP) and molybdenum dithiocarbamate (MoDTC) have been widely reported, yet that from ILs and NPs need to investigate further. This review serves as a reference for researchers to design and optimize new lubricants.

Keywords: lubricant additives; tribochemical reactions; oil-soluble organics; ionic liquids (ILs); nanoparticles (NPs)

1 Introduction

Additives are essential components in high-performance lubricants [1–3]. The best way to prevent wear and reduce friction is to separate the contacting surfaces in moving parts. Fluidic forces can carry out this separation at sufficiently high speeds and low loads, or with a tribochemically formed film [4]. The tribochemically active additives can separate the surfaces in the boundary lubrication regime by forming solid or viscous thin films [4, 5]. These tribochemical reactions can significantly improve the overall performance of a lubricant. In some conditions, it can even make macroscale superlubricity possible [6, 7].

Products induced by tribochemical reactions due to additives develop a thin film called the tribofilm [4, 8]. This tribofilm was first found in zinc dithiophosphates

(ZDDP) [8]. Initially, ZDDP was used as an anti-corrosion additive in lubricating oil [9]. It was later found that lubricant with ZDDP added produced a thin film on the lubricated surfaces. This thin film increased the wear resistance of the lubricated surfaces despite its mediocre friction behavior [10]. Later, other additives that could also tribochemically form thin films with different tribological behaviors were found [3, 11–13]. In Fig. 1, the development of a few widely reported additives was shown chronically.

Understanding tribochemical reactions has evolved since the 1980s (Fig. 1). ZDDP was the first lubricant additive whose tribochemical process was studied. The importance of tribological conditions was also discovered in the early reports. From the late 1980s to 1990s, new surface characterization methods greatly improved the understanding of tribochemical reaction

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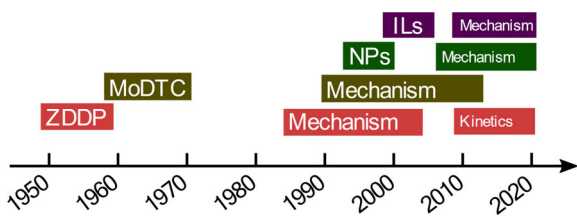


Fig. 1 Development of tribochemically active lubricant additives, their reaction mechanisms, and underlying thermal dynamic principles.

mechanisms. This also improved the understanding of other tribochemically active lubricant additives such as molybdenum dithiocarbamate (MoDTC). In the 2000s, the popularization of molecular dynamics methods further improved the elucidation of tribochemical reaction mechanisms. The development of two novel lubricant additives, ionic liquids (ILs) and nanoparticles (NPs), also occurred in this decade, although their reaction mechanisms were not studied until the 2010s. During this time, the kinetics of tribochemical reactions also started development. However, that research mostly focused on the reactions of ZDDP. Tribochemical reactions of lubricant additives were also studied in a case-by-case manner. To date, no universal principles or reaction routes have been proposed for all the tribochemically active lubricant additives. By reviewing the tribochemical process of these lubricant additives, their common features can be summarized. The result of this review will help the development of more effective lubricant additives.

In this paper, the thermodynamics and kinetics of tribochemistry are focused. Three different kinds of tribochemically active lubricant additives are discussed: ZDDP and similar metal organic lubricant additives, tribochemically active room-temperature ILs, and the most recent development in this field, NPs and their tribochemical reactions.

2 Some basic concepts of tribochemistry

2.1 Thermodynamic aspects of tribochemistry

Thermodynamic principles have been used to analyze the tribochemical reactions of lubricant additives since they are under a controlled contact pressure. When the Gibbs free energy change of a reaction is negative,

the reaction is considered spontaneous. The analysis of the Gibbs free energy (ΔG) often breaks it down to two parts: the change of entropy (ΔS), and the change of enthalpy (ΔH) [14]:

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where T is the temperature. Here, the change of enthalpy can be interpreted as the energy change due to the alteration of chemical bonds or material structures. The change of entropy represents the energy penalty for making the system more ordered under a certain thermal agitation (a more detailed and physically strict interpretation can be found in many thermal dynamic textbooks). Equation (1) states that at a fixed pressure, a reaction is possible when the thermal energy released by changing the chemical structures and atomic orders exceed the energy of thermal agitation. The Gibbs free energy has been used to explain the formation of ZDDP-involved tribofilms [15].

The chemical reactions during tribological contact cannot be fully described by thermodynamics theory in equilibrium or reversible state. These tribochemical reactions of lubricant additives have three unique conditions that demand modification of the Gibbs free energy: the surface energy from the interface of lubricant and lubricated materials, the thermal and mechanical agitation from the friction force, and the change of free energy induced by shear strain. Here, the influences of these three factors are discussed.

2.1.1 Surface energy

Surface energy must be considered in tribochemical reactions because these reactions are confined to a small space. The tribological lubricant film has a thickness of a few microns, and the boundary films are on the submicron scale. The contact between asperities allows the reactions to happen in a space only a few atomic layers thick. In all the three conditions, the surface-to-volume ratio is too high to be not considered. To account for the surface energy, Eq. (1) needs to be modified to Eq. (2):

$$\Delta G = \Delta H - T\Delta S + A\gamma \quad (2)$$

where A is the contact area, and γ is the surface tension between lubricant and contacting surfaces.

Surface energy is the cause of the adsorption of lubricant additives. In the tribochemical reactions, the surface (interface between oil and metal solid) area is a constant. Hence, we only need to consider the change of γ . The adsorption of lubricant additives occurs because it lowers the surface tension on the lubricated surfaces. All tribochemical reactions reviewed in this paper started with the adsorption process. For example, ZDDP can be chemically adsorbed on metal and metal oxide surfaces through the ion exchange process. The room-temperature ILs can be adsorbed on the metal surface via electrostatic forces. Water molecules adsorbed on a silica surface can even lead to ultra-low friction through tribochemical reactions [16].

Another less frequently discussed effect of surface energy on tribochemical reactions is its effect on lubricant and lubricant additives. When confined between two nascent metal surfaces, ILs can transform from fluid to viscous solid. The solid phase of IL has lower metal–IL interface energy compared to the liquid phase, promoting this transformation.

2.1.2 Frictional heating

The friction force is dissipative, meaning that the energy created by $f \cdot \text{distance}$ (f is the friction force) is dissipated from the contact to the surrounding materials. This can create a large thermal gradient [17–19]. Under dry sliding, this thermal energy can even change the microstructure of the contacting metal [18]. In the case of boundary lubrication or single asperity contact, this thermal gradient is considerable [17]. This friction energy can increase the local temperature at the contact region, which can change the fluid film thickness in the elastohydrodynamic (EHD) lubrication regime [20]. For tribochemically active lubricant additives, the localized temperature can increase its reaction rate. The very localized high temperature also creates a large thermal gradient. This can cause the diffusion of molecules along this thermal gradient or polarization of some molecules [21].

2.1.3 Energy due to fluidic shear

To analyze the influence of shear stress, extended irreversible thermodynamics can be used. The major

“extension” that these thermodynamics make is the re-introduction of the concept of “space”. In equilibrium thermodynamics, the systems that we analyzed were all ambiguous entities without a clear shape or position. The extended irreversible thermodynamics studies a “space” that has positions. Assigning external quantities such as entropy, free energy, volume, and chemical compositions to a “position” creates two new things. One is the “flux” such as energy flux and diffusion flux of matter. The entropy, being a non-conservative quantity, has an explicit “rate of production” and entropy flux (heat flux). Similar to the extensive quantities turned into fluxes, the introduction of positions makes intensive quantities turn into “forces”. The second equation of thermodynamics was reinterpreted here as “the fluxes and the forces must make the entropy production be positive”. The flow of liquid under shear stress inside the tribological contact creates an open system. This open system can be analyzed in the same way as the thermal gradient by creating a “flux” term.

The shear stress can increase the free energy. A rough analysis can lead to Eq. (3) of the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S - V\Delta J_{\text{flow}} \tau_{\text{visco}}^2 \quad (3)$$

where V is the volume, τ_{visco} is the shear stress in fluid, and J_{flow} is the steady flow compliance defined as $J_{\text{flow}} = \frac{G'}{G''^2}$ when the frequency is 0 Hz [22]. G' and G'' are the storage and loss components of the shear modulus G , respectively. Equation (3) tells us the creation of a matter with a higher storage modulus is favored under a high shear stress.

2.2 Kinetics of tribochemical reactions

Tribochemical reactions can be triggered by frictional heat and/or triboemission. When there is sliding between two contacting surfaces, the frictional force can generate a significant concentrated force, which creates a phenomenon called frictional heat. Triboemission is the emission of electrons, charged particles, and photons caused by abrasion [23]. These emitted particles can promote electrochemical reactions

and act as catalysts [24–26]. The effect of triboemission, typically the triboemission of charged particles, is essential to the tribochemical reactions in the boundary lubrication regime [24].

Without triboemission, the shear force can change the kinetics of tribochemistry as well. Experiments conducted with the atomic force microscopy (AFM) show that the simple pulling force is sufficient to trigger the disulfide bond reduction [27]. The force applied to the molecules deforms the molecular structures, thus changing the reaction characteristics. This can be modeled as the change of activation energy. In the tribochemical reactions, this mechanochemical process occurs on the molecules adsorbed on the contacting surfaces that are distorted by the shear stress between two contacting surfaces [28].

Strain on the molecule can directly change the kinetics of reactions. Thiol/disulfide exchange reaction's reaction rate can be controlled by stretching the disulfide bond with the AFM [27]. It was found that the reaction rate of this reaction increases exponentially with the applied force. Activation energy was shown experimentally to reduce by 8.2 kJ/mol under 400 pN force on the S–S bond [27]. In addition, the effect of force and temperature also indicated that the force applied on the S–S bond changes its activation energy [29]. The reaction rate r can be expressed as the Arrhenius equation [29]:

$$r = Ce^{\frac{E_a - F\Delta x_r}{k_B T}} \quad (4)$$

where C is the pre-factor, F is the force applied on the bond, E_a is the activation energy, k_B is the Boltzmann's constant, and Δx_r is a factor with a dimension of length. A direct result of this relation is that pulling of the molecule increases the reaction rate in a similar manner to increasing temperature, as shown in Fig. 2 [29].

Mechanochemical effects on reaction rates not only applied to the molecules directly pulled by AFM but also on the surface adsorbed molecules under shear [28]. Similar to the direct pulling of the molecules, the reaction rate increased with the increase of applied shear force. In the studies of methyl thiolate decomposition activated by shear force [28], molecular dynamics simulation shows that

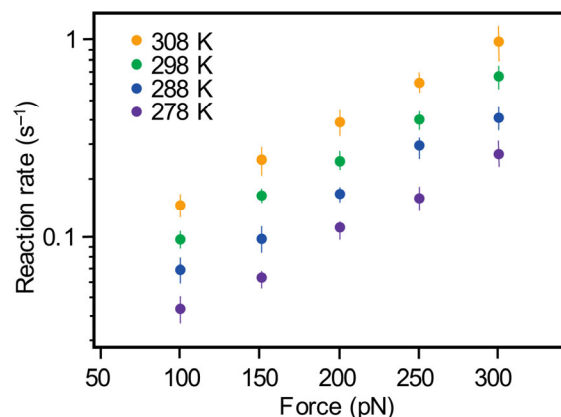


Fig. 2 Reaction rate of S–S bond reduction under the influence of force and thermal energy. Redraw using data in Ref. [29], © American Chemical Society 2011.

the adsorbed molecules experienced a normal force under constant shear. This normal force was distributed on the surface molecules, changing their chemical reactivities.

The microscopic origin of this activation energy function shift under shear is the change of bond length distribution. Figure 3 displays the calculated bond length distribution of a surface-adsorbed allyl alcohol molecule [30]. This shows that the bond length distribution “flatten” during sliding, decreasing the energy required for bond breakage. The change of molecular configuration under shear force can also transfer the atoms on the contacting surfaces and make it react with the adsorbed molecules [31].

The kinetics of tribofilm growth can also be modeled as Eq. (5) [32–34]:

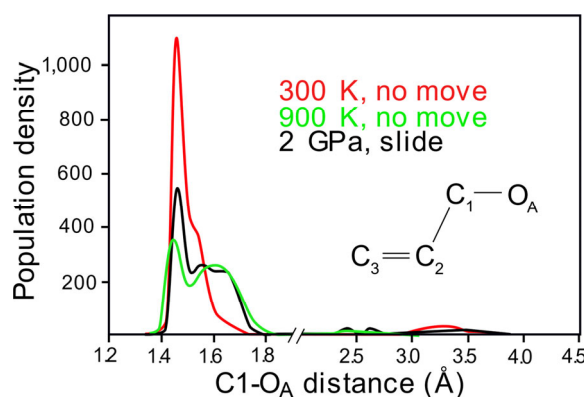


Fig. 3 Bond length distributions of a C1–O_A bond in the adsorbed allyl alcohol under room temperature, 2 GPa shear stress at room temperature, and high temperature. Replotted using data from Ref. [30], © American Chemical Society 2016.

$$\left(\frac{\partial h}{\partial t}\right)_g = \Gamma_0 e^{\frac{E_a - \tau \Delta V_{act}}{k_B T}} \quad (5)$$

where h is the thickness of the tribofilm, Γ_0 is a pre-factor, τ is the shear stress defined by $\tau = \mu p$ (μ is the coefficient of friction (COF), and p is the contact pressure), and E_a is the activation energy. This shear stress is a function of load, entrapment speed, and oil properties, which indicates that the test and operate conditions affect the tribochemical reactions. This will be further discussed in Section 3 on ZDDP and other additives. In order to make the grouping $\tau \Delta V_{act}$ have the same dimension as energy, ΔV_{act} has the same unit as a volume. It was called “activation volume” in some reports relating the dimensional factor being activated.

In Ref. [35], Eq. (5) takes another form:

$$\left(\frac{\partial h}{\partial t}\right)_g = \Gamma_0 e^{\frac{\Delta U_{act} - \Delta E}{k_B T}} \quad (6)$$

In Ref. [35], a term called mechanical energy input ΔE is defined. Since this “mechanical energy” term is linearly proportional to the shear stress defined in Eq. (5), these two definitions are mathematically identical.

This simplistic model cannot explain some phenomena in tribofilm growth. The Arrhenius equation will always produce a positive growth rate, which is not true. For example, the growth of ZDDP tribofilm can be described with three phases: growth, slight decrease, and then stabilized at a certain thickness. Even in the stable growth phase, the growth rate of tribofilm is not constant [36]. For the mechanisms which limit the thickness of tribofilm such as wear, consumption of iron must be considered.

The deviation from the simple Arrhenius behavior can be explained by three factors. First, shear stress or mechanical energy input is not a constant factor during the growth of tribofilm due to the evolution of contact pressure [32, 37]. Second, the growth of tribofilm may require multiple steps; each has a different activation energy and activation volume [15]. Third, tribological forces also cause the wear of the generated tribofilm. The balance of these three mechanisms have made the modeling of the tribochemical process difficult [32].

3 Tribochemical reactions involved with lubricant additives

3.1 Reactions with ZDDP

The characteristics of tribochemically formed thin films are essential to anti-wear and friction modifying lubricant additives. These additives include organo-sulfurs, organo-chlorine, and organo-phosphorus [38]. Among these, the most adapted ones are three chemical groups, ZDDP, MoDTC, and molybdenum dithiophosphate (MoDTP).

The phosphorus and sulfur-based anti-wear and friction modifying chemicals are widely used as lubricant additives. One of the most important anti-wear additives, ZDDP, was introduced in the 1930s, first as corrosion and oxidation inhibitors in lubricant oil [2, 39–42]. At that time, the idea of using phosphorus and sulfur-based corrosion inhibitors was quite popular; many similar chemicals were developed [43, 44]. ZDDP’s anti-wear property was unnoticed for 20 years before it became the most popular anti-wear additive [2, 45].

The chemical structure of ZDDP is important for the formation of its tribofilm. In Fig. 4(a), the most widely used ZDDP structure is shown [46]. Here, the Zn represents zinc, and the R represents the alkyl chain [46, 47]. The ZDDP in lubricant oil can form a chelate with a structure shown in Fig. 4(b) [46, 47]. In lubricant oil, the two forms of ZDDP are in equilibrium. The decomposition of this dithiophosphate structure enabled its formation of the tribofilm. Other metal ions can also form dithiophosphate, but none of them have better anti-wear properties than ZDDP [48]. The alkyl chain composition and configuration of ZDDP have little to no influence on its anti-wear

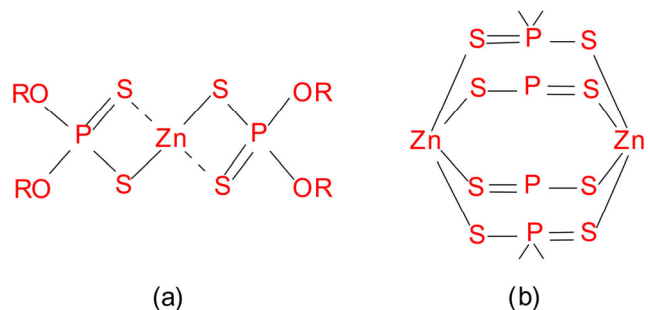


Fig. 4 Possible structures of ZDDP in lubricant oil. Reproduced with permission from Ref. [46], © Elsevier Science S.A. 1997.

performance [48, 49], even though it can influence its other functions like dispersant or detergent [49].

ZDDP can form tribofilms quite easily. It can form tribofilms when fully decomposed [50], under room temperature [51], from pure EHD contact [51], and from single asperity contact [34, 37], even when Zn is replaced with other metal ions [49]. The final product can also vary based on the conditions and R groups in ZDDP. It can be long-chain polyphosphate [52] or short-chain polyphosphate [53], containing Zn or Fe, or only containing Zn [50, 54, 55]. These different applicable conditions render the reaction mechanism rather complex and can happen concurrently.

Surface chemistry also plays an essential role in tribochemical reactions. Tribochemical reactions of lubricant additives cannot take place without adsorption. ZDDP decomposes on the surface at a lower temperature compared to its decomposition in bulk fluid [50] even without rubbing.

Multiple tribochemical reaction routes have been proposed. Table 1 lists four proposed mechanisms of ZDDP tribochemical decomposition and film formations. There are three major differences between these chemical reaction routes. First, the reactant adsorbed on the surface of the metal. Early studies all assumed ZDDP directly adsorbed on the surface and decomposed. However, X-ray absorption near-edge structure (XANS) experiments found out that the linkage isomer of ZDDP (LI-ZDDP, which has a formula of $Zn[O_2P(SR)_2]_2$) is formed [50] or adsorbed [56, 57] on the metal surface before the tribochemical reactions. ZDDP tribofilm contains a certain amount of iron, but only some tribochemical reaction routes involve the metallic oxide [54, 58]. In addition to this, the final product is different. Some proposed the formation of long-chain polyphosphate, and others proposed the formation of short-chain polyphosphate. One study points out that ZDDP decomposed in solution always forms a colloidal short-chain polyphosphate, and the short-chain polyphosphate was the product of the colloidal adsorption [50].

To analyze these reaction routes, the reacting steps are classified based on the change in molecular structures. Based on this, some common features appeared in these proposed chemical routes. In Table 1, all the chemical routes are classified into four steps.

Table 1 Reported chemical reaction routes of ZDDP under tribological forces.

Year	# of steps	Adsorbed reactant	Metallic oxide	Intermediate	Final product	Data source	Ref.
1995	4	ZDDP	No	$(RO)_2P(S)OH$, $(RO)_2P(S)OR$	ZnS, $(HO)_3P(O)$	[56, 59–61]	[58]
1997	3	ZDDP	Yes	Zinc metaphosphate, $Zn(PO_3)_2$	$FeZnP_2O_7$, $Fe_2Zn(PO_4)_2$	[4, 58, 62]	[63]
1998	5	ZDDP, LI-ZDDP, colloidal polyphosphates	No	LI-ZDDP, $Zn(PO_3)_2$ (polyphosphate)	$Zn_7(P_5O_{16})_2$, Zn_2PO_7 , $Zn_3(PO_4)_2$	[56, 57, 63, 64]	[50]
1999	2	ZDDP	Yes	—	Polyphosphate modified with zinc and iron(II)	[50, 65]	[66, 67]

First, the adsorption of ZDDP. The sulfur atom on the P–S bond can be adsorbed on the metal surface via electron exchange or ligand exchange [68]. Second, the migration of an alkyl chain from an oxygen atom to a sulfur atom (from $-S-O-R$ to $S-R$). Third, the $S-R$ detaches from the adsorbed molecule. Last, the polymerization of the remaining molecules occurs by the detachment of sulfur-bonded phosphorus chemicals. In other words, these four chemical processes are essential to forming polyphosphate from ZDDP. A detailed analysis of the free energy of various intermediates in ZDDP decomposition can be found in Ref. [15].

3.1.1 Decomposition of ZDDP

ZDDP is not a thermally stable chemical and can easily decompose at elevated temperatures [50]. The ZDDP tribochemical or thermal decomposition is often called a “self-reacting” process. ZDDP can decompose in non-polar solutions at 100 °C, and when rubbed, it can decompose at room temperature [51]. The quantum chemical calculation shows that the Gibbs free energy of zinc polyphosphate is 10.7 kcal/mol lower than that of the ZDDP at 500 K [15]. Thus, it can decompose freely.

One chemical principle called “hard” and “soft” acid and base has been used to explain why ZDDP tends to decompose and form phosphate compounds [56, 69]. The concept was supported by experiments

and the first principles calculations [70]. In this theory, the reactive nucleophiles (base) and electrophiles (acid) can be split into “hard” and “soft” categories according to their charge and polarizability. In the context of ZDDP tribochemical decomposition, there are four chemical groups involved, which are carbon, phosphorus, thiophosphoryl (P=S), and phosphoryl (P=O). The categorization is listed in Table 2. The “hard” and “soft” acid and base theory states that “hard acid” tends to react with “hard base”, and “soft acid” tends to react with “soft base”. Thus, the alkyl chain (tetravalent carbon) tends to attach to the sulfur in thiophosphoryl instead of oxygen. In the same principle, the phosphorus joins to the oxygen in the phosphoryl group, forming the final product polyphosphate. This “hard” and “soft” base and acid theory explained why the final product was predominately polyphosphate.

3.1.2 Composition of ZDDP tribofilm

Much of the early debate over the ZDDP tribochemical mechanism has resulted from the lack of knowledge of the tribofilm’s microstructure and composition. Early research only considered the final product to be a “phosphorus glass”. The studies conducted from the late 1990s to 2000s show a tribofilm with a complex microstructure, which had a high degree of heterogeneity. It turns out that the reactions proposed by different studies (Table 1) are not mutually exclusive. They in fact happened more or less concurrently, leading to the final composition.

The fully-formed ZDDP tribofilm has four regions. At the very top of the tribofilm are the adsorbed alkyl chains [62]. Underneath this adsorption layer is a thin layer (about 10 nm) of long-chain zinc poly(thio)phosphate. The bulk of the tribofilm, what the older literatures refers as “phosphorus glass”, is short-chain polyphosphate containing metal oxide/sulfide (about 100 nm). The tribofilm displays alteration in the topography of contact area by increasing

Table 2 Hard–soft acid–base categorization of moieties in ZDDP.

	Acid	Base
Hard	Tetravalent phosphorus	Phosphoryl (P=O)
Soft	Tetravalent carbon	Thiophosphoryl (P=S)

its roughness [71]. In Fig. 5, the cross-section of a ZDDP tribofilm is shown [2]. It should be noted that the thermofilm does not contain this oxide layer [50]. This, combined with the fact that there is more long-chain polyphosphate in tribofilm [50], may explain some mechanical behavior differences between the two. Tribofilm has better wear resistance compared to the thermofilm [65]. The nanoindentation hardness of ZDDP reaction films formed tribochemically was two times stronger than that of a thermally formed one [72]. Moreover, the tribofilm formed at lower temperatures contained longer polyphosphate chains, resulting in a stronger film [73].

Although the decomposition of ZDDP does not require the assistance of ferrous wear debris [74], the substrate influences its decomposition process. The substrate can affect the absorption process of ZDDP. The substrate with better ZDDP absorption, such as steel, has a thicker tribofilm formed compared to SiC or DLC in the same tribological conditions [75].

3.1.3 Kinetics of ZDDP tribofilm growth

Among different lubricant additives, the tribochemical kinetics of ZDDP decomposition is the only well-studied one. Aside from its importance in lubricant engineering, several factors render the feasibility of the kinetics study. ZDDP tribochemical decomposition forms a stable tribofilm with a relatively uniformed thickness. The thickness of ZDDP tribofilms is in the range of 100 nm. It can be measured with the optical or AFM methods with ease.

The growth rate of ZDDP tribofilm is a function of the concentration of ZDDP, temperature, ZDDP alkyl chain, and the shear stress in the contacted region [32–34, 36, 51, 76–78]. The concentration of ZDDP can change both the ZDDP tribochemical reaction rate and the equilibrium tribofilm thickness [76]. It was found that at low concentrations (<0.2 wt%), the growth rate is proportional to the square root of

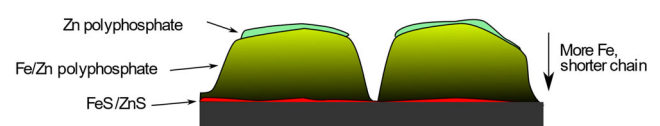


Fig. 5 Cross-section image of ZDDP tribofilms. Reproduced with permission from Ref. [2], © Springer Science+Business Media, Inc. 2004.

ZDDP concentration [76]. Like many other chemical reactions, the ZDDP tribochemical reaction follows the Arrhenius equation, e.g., the logarithm of growth rate is inversely proportional to the temperature [34, 76]. The ZDDP alkyl chain type can change the reaction rate. Secondary ZDDP can form a thicker film more rapidly compared to primary ZDDP [76]. The quantum chemical study shows that the type of alkyl chain determines the reaction routes [15]. Tribochemical kinetics of ZDDP is also controlled by the shear stress on the contacting surface. This stress is defined by multiplying the contact stress with the COF [33, 79]. Several molecular dynamics studies have revealed that the shear stress on rubbing surfaces stretches sulfur and phosphorous covalent bonds [80, 81]. This stretching lowers the thermal energy required for bond cleavage, thus accelerating the ZDDP tribochemical reaction speed.

The wear or removal speed of ZDDP tribofilm is generally considered a function of both ZDDP tribofilm

thickness and contact pressure [32, 37]. Other lubricant additives such as dispersant and detergent and humidity in lubricant increase the wear rate of ZDDP tribofilm [51, 82]. This wear or removal process is also present in the EHD lubrication regime where no real contact occurs, indicating that the wear of the ZDDP tribofilm may be a tribochemical decomposition process. Different ZDDP tribochemical reaction models are listed in Table 3.

The ZDDP tribochemical kinetics studies are also valuable to the additive tribochemical reactions in general. First, these studies indicate which parameters are important in a study of tribochemical reactions. Some early research [34, 76] for ZDDP omitted the friction force, which was later proven to be critical to the kinetics of tribochemical reactions. The critical parameters for an additive tribochemical kinetics study are the concentration of the additive, shear stress in the contacted area, and temperature. Second, the thickness of a tribofilm is determined by a chemically

Table 3 Tribochemical kinetics models for ZDDP growth.

Model	Parameter	Equationing	Lubrication regime	Ref.
$\left(\frac{dh}{dt}\right) = h_{\max}(k_1(1-X) - k_5X^4)$	h —ZDDP tribofilm thickness h_{\max} —maximum tribofilm thickness k_1 —formation constant k_2 —removal constant	Curve fitting	Mixed	[51]
$\left(\frac{dh}{dt}\right)_{\text{growth}} = C_1(h_{\max} - h)\exp\left(-\frac{C_2}{\mu p v}\right)$ $\left(\frac{dh}{dt}\right)_{\text{wear}} = \kappa p v$	h_{\max} —final thickness μ —COF p —contact pressure C_1, C_2 —fitting parameters v —relative surface velocity $\mu p v$ —frictional heat κ —Archard wear coefficient	Arrhenius growth and Archard wear	Boundary	[83, 84]
$\left(\frac{\partial h}{\partial t}\right)_{\text{growth}} = \Gamma_0 \exp\left(-\frac{\Delta U_{\text{act}} - \tau \Delta V_{\text{act}}}{k_B T}\right)$ $\left(\frac{dh}{dt}\right)_{\text{wear}} = \alpha h$	ΔU_{act} —activation energy ΔV_{act} —activation volume τ —shear stress k_B —Boltzmann’s constant T —temperature α —fitting parameter	Arrhenius growth	Boundary lubrication	[32]
$h = h_{\max} \left(1 - \exp\left(-\frac{k_1 T}{h'} \chi_{\text{tribo}} t\right) - C_3(1 - \exp(-C_4 t))\right)$	h_{\max} —maximum tribofilm thickness k_1 —formation constant h' —thickness constant T —flash temperature χ_{tribo} —initiation factor C_3, C_4 —fitting parameters	Arrhenius growth and Archard wear	Boundary lubrication	[79, 85, 86]

controlled tribofilm growth process and a tribologically controlled wear process. Third, the tribochemical reaction may be triggered by both asperity contact and high fluid shear stress. The tribochemical reaction of a certain lubricant additive should be investigated on different lubrication regimes.

3.2 Reactions with MoDTC

Similarly structured Molybdenum sulfur-based compounds were introduced in the 1970s such as MoDTC and MoDTP [87]. These compounds can form tribofilms containing MoS_2 solid lubricant, making it also a friction modifier [11, 87–89]. Other metal ion sulfides/phosphates with similar structures can also be used as an anti-wear additive with worse anti-wear effectiveness [49]. Interestingly, such chemicals can also be synthesized *in-situ* through the tribochemical process [90]. Unlike ZDDP, the tribofilm formed by MoDTC and MoDTP contains solid lubricant MoS_2 . However, the low shear strength of MoS_2 makes the MoDTC and MoDTP tribofilm prone to wearing out. Without constant resupply of MoDTC, the low friction cannot be maintained. Compared to ZDDP, MoDTC also has a “fast” tribochemical reaction. The friction modifying effect was almost immediate when MoDTC was added to the lubricating oil [91].

MoDTC, MoDTP, and similar compounds (sulphurized oxymolybdenum organophosphorodithiolate) were developed in an effort to create an “oil soluble” MoS_2 in the 1970s [92, 93]. The additional friction modifying effect of these compounds combining with the “solubility” made it quite desirable at that time [93]. Not until nearly a decade later did people realize that their friction modifying property was not because they are a “soluble” MoS_2 , but because they can tribochemically generate MoS_2 on the surface of the rubbed surfaces [11, 94].

MoDTC decomposition without rubbing requires a high temperature of 300 °C [92], while under tribological conditions, it can be decomposed even under room temperature [95]. Under a higher temperature of 100 °C, the decomposition of MoDTC/MoDTP can form MoS_2 single sheets that greatly reduce the COF (Fig. 6) [94, 96]. It was also found that MoDTC has better performance compared to MoDTP [11]. This paper will focus more on MoDTC

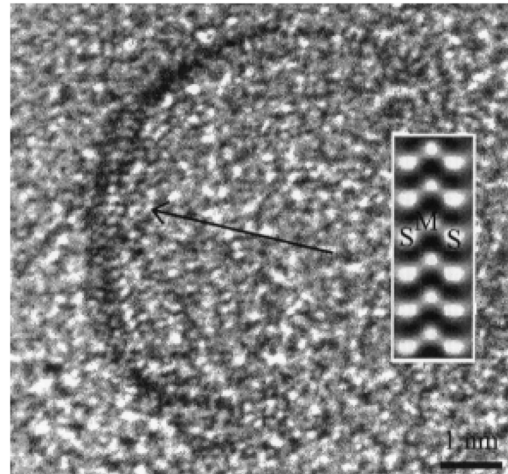


Fig. 6 Cross-section image of MoDTC tribofilm under TEM. The close-up image shows the two-dimensional (2D) MoS_2 . Reproduced with permission from Ref. [96], © Elsevier Science Ltd. 1999.

tribochemical reactions because it is a more researched topic. This crystallized tribofilm is diametrically different compared to the amorphous phosphate film generated by metal thiophosphates.

Here, a new phenomenon that did not occur in the case of ZDDP is present. It is the transferring of 2D MoS_2 particles to the rubbed surfaces. In the fully formed MoDTC tribofilm, MoS_2 was nearly all present on the surface of the tribofilm. In ideal conditions, this transferring can create an ultralow COF < 0.01 [94].

In contrary to the tribochemical product of ZDDP, there has been little debate on the final product of MoDTC. This lack of controversy was also a result of the similarity between the reactant and the product. The MoDTC already has a sulfur atom attached to the molybdenum atom. Thus, the focus of the previous research was on how the oxygen attached on the molybdenum atom was replaced by the sulfur atom.

The research in the late 1990s proposed the route of MoDTC tribochemical decomposition [96]. It was proposed that MoDTC on the rubbed surface first decomposed into two free radicals. The growth of MoS_2 2D particles was the result of oxidation of the Mo-containing free radical [96]. This reaction is shown in Fig. 7. This route, however, cannot explain why MoDTC performed better under vacuum with metals stripped of an oxide layer [94]. Also, later research [97] using a newly sputtered iron surface under ultra high vacuum (UHV) proved that the decomposition

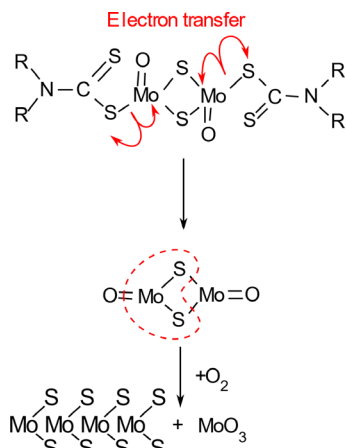


Fig. 7 Mechanism of MoDTC tribochemical reaction by oxidation. Reproduced with permission from Ref. [96], © Elsevier Science Ltd. 1999.

of MoDTC does not need the involvement of oxygen. In addition to that, the presence of oxygen can greatly hinder the formation of MoDTC tribofilm [98]. Thiuram disulfide was also not present in the final product, as the final MoDTC tribofilm was more of a “carbon matrix” [11].

The molecular dynamics simulation of MoDTC tribochemical reaction proposed another route. It was concluded that the MoDTC first became a linked isomer (LI-MoDTC), because its Gibbs free energy and the transitional state’s Gibbs free energy is lower than that of the intermediate Mo free radical proposed by the previous reaction [99]. The adsorbed LI-MoDTC is shown in Fig. 8. The simulated result shows that this chemically adsorbed molecule will further decompose under tribological forces. The first bond to break was the Mo–O bond; this directly forms an MoS₂ along with thiocarbamic acid [100]. This route explains why MoDTC can tribochemically react with the nascent iron surface in a vacuum because it does not require the involvement of oxygen.

The mechanism of the “transferring” of MoS₂ single sheets was later elucidated with molecular dynamics simulation [101]. This simulation started with the randomly arranged MoS₂ molecules pressed down on the surface of iron (no oxides). After the shear force was applied, the 2D-ordered MoS₂ single sheets formed in only 0.1 ns [101]. Another reason for this “transfer” to happen is the MoS₂ single layer can bond to the iron surface via electron exchange [102]. This result shows that the single sheet MoS₂ was more

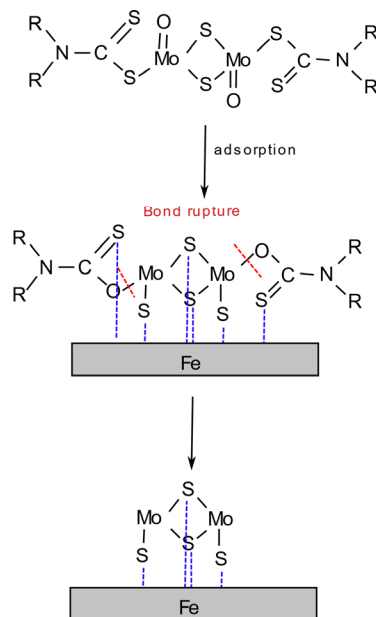


Fig. 8 Mechanism of MoDTC tribochemical reaction by decomposing to LI. Reproduced with permission from Ref. [99], © Japanese Society of Tribologists 2008.

stable under tribological conditions. The amorphous phase can also be present in other organo-molybdenum compounds. In the tribochemical reaction of amide molybdate, MoS₂ amorphous phase can form under low contact pressures [103].

3.3 ILs

Room-temperature ILs are a type of ionic salt in the liquid phase under room temperature. The ions of ILs are mostly large organic molecules. Due to their molecular size and chemical properties, the electrostatic force between their cation and anions is low, thus being a liquid at room temperature.

ILs have many favorable properties such as high thermal stability [104, 105], low volatility, and high miscibility with an organic solvent [106, 107], making them good choices for both lubricants and lubricant additives [108, 109]. In addition, the ILs also present some physical properties, which enable them to “separate” the contacting surfaces when used as a lubricant or lubricant additive. ILs can solidify when confined by metal to a nanometer scale [110]; they also introduce the double layer force when adsorbed on the metal surfaces, and most importantly, they are tribochemically active, readily decompose, and form a tribofilm when rubbed on metal or metal oxide surfaces.

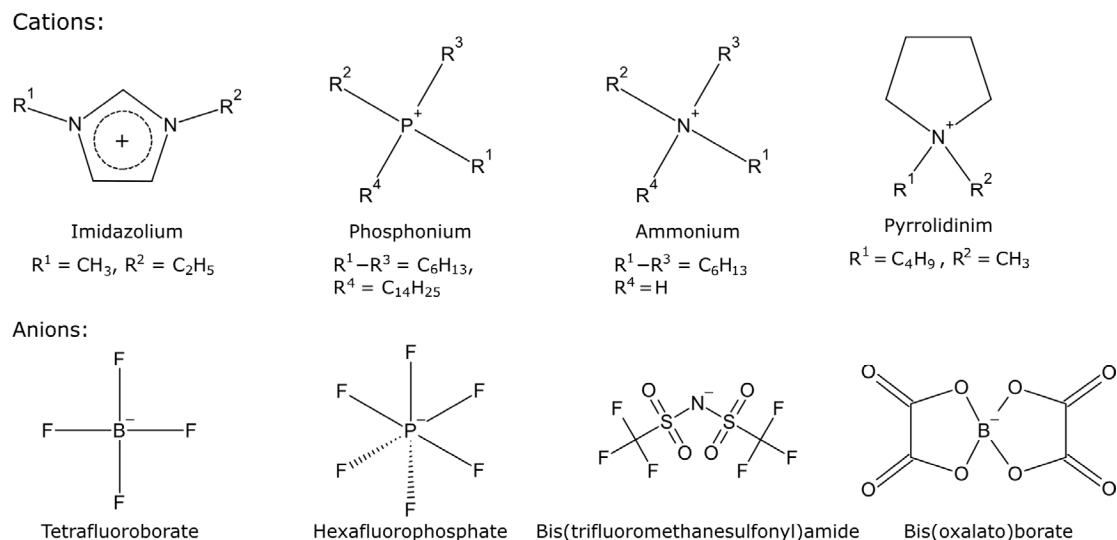


Fig. 9 ILs commonly used as lubricant additives. Reproduced with permission from Ref. [111], © the authors 2013.

The chemical structures of ILs determine their tribological behavior and physical characteristics [109]. Unlike the metal phosphate/sulfide additives discussed in Section 3.1, the chemical structure of IL has two parts: cations, which are positively charged; and anions, which are negatively charged. Both the cations and anions have a structure, which consists of a charged “head” and an alkyl chain or fluorocarbon chain, as illustrated in Fig. 9. The most important aspect of ILs in the context of its tribochemical behavior is their charge-carrying atoms. As shown in Table 4, the typical cations in IL lubricant additives’ ions can be categorized by their tribochemically active elements.

Like the phosphate/sulfate tribofilm-forming anti-wear additives, IL molecules adsorbed on the metal surface decompose and form a tribofilm under tribological forces. The ions in the ILs can be adsorbed on the metal surface with the ionic “head” attached to the surface [106, 112]. This alone can reduce the COF under moderate load [113].

Both anions and cations of the ILs participated in the tribochemical reactions on the metal surface [112, 114]. In contrast to the adsorption-dominated-low-load-friction reduction, the tribochemical reactions dominated the friction reduction at a high load range [112, 115]. The composition of the tribochemical reaction product was directly related to the element carrying the charge. Unlike MoDTC and ZDDP, the alkyl chain had little influence on the composition of

tribofilm and did not participate in the tribochemical reaction. The only exception was the fluorinated cations, which produced the metal fluoride in tribochemical reactions [116]. The nitrogen-containing ILs produced metal nitrides [117], the phosphorus-containing ILs produced metal polyphosphates, and the sulfur-containing ILs produced metal sulfides [115].

IL-containing ions such as phosphonium or phosphate can tribochemically react to form a tribofilm, much like the ZDDP tribofilm [116, 118]. Like ZDDP, the phosphate in the IL reacts with iron to form iron phosphate. Phosphorus-containing ILs cannot self-react and form a film like ZDDP [116]. The tribofilm reaction of a typical phosphate-containing IL requires the involvement of iron oxide and wear debris. The growth of the film can also encapsulate the wear debris into the formed tribofilm [116]. This also resulted in the thickness of the IL tribofilm being about 50 nm, thinner than that of the ZDDP [116]. When both fluoride and phosphorus were present in an IL, it seemed that both metal fluoride and metal phosphate appeared in the tribofilm at low loads, but only metal fluoride appeared in the tribofilm at higher loads [117, 119].

The carboxyl anions, while not tribochemically active, can influence the tribochemical reaction of the cation [116]. The phosphonium carboxylate IL can form a thicker phosphate tribofilm compared to the phosphonium organophosphate tribofilm, despite the latter containing more P in its structure [116].

Table 4 ILs commonly used as lubricant additives and their tribochemically active elements.

IL cation	Tribochemically active element
Imidazolium	N
Phosphonium	P
Ammonium	N
Pyrrolidinium	N
IL anions	—
Fluoroborate	B, F
Fluorophosphate	P, F
Phosphate	P,
Borate	B
Fluorosulfonylamide	N, S
Carboxylate	—

In contrast, the carboxylate anions prevented the tribochemical reaction of imidazolium cations to form a metal nitride tribofilm, which had a high COF [120].

Unlike ZDDP or MoDTC, most ILs used as additives or lubricants have excellent thermal stability [121]. They decompose at a higher temperature than polyalphaolefin (PAO) [118, 121]. Because of this stability, the self-reaction is unlikely to occur even with the help of tribological forces. In addition, nitrogen, phosphorus, and sulfur carry the ionic charge. When adsorption occurs, they will directly attach to the metal or oxide surface.

The tribochemical reaction of the IL also requires the metal or oxide surface. The product of the tribochemical reaction of ILs is metal polyphosphate. Most ILs do not contain any metallic elements. They must react with metal surfaces or wear debris. This

also causes the tribofilm formed by ILs to contain a metallic core.

Although the alkyl chain does not directly participate in the tribochemical reactions and does not appear in the tribofilm, the length of it can affect the IL's adsorption behavior and the tribochemical reaction rate. In the research on alkylimidazolium IL [122], it was found that the ILs with longer alkyl chains can better adsorb on the contacting surfaces and formed a tribofilm more effectively. However, another article [114] using similar alkylimidazolium IL on nascent steel surface found the opposite result: the longer the alkyl chain, the slower the tribochemical reactions. This seemingly contradictory result may indicate that the IL's adsorption behavior on metal and metal oxides is different.

The COFs of IL tribofilms were 0.1–0.2, similar to that of the lubricant with ZDDP as additive. When ILs with P were used, their tribofilm compositions were also similar. Both contain polyphosphate. The only difference is that ZDDP tribofilm contains zinc, and IL tribofilm encapsulates some wear debris.

Because of its solubility in water, ILs can be used as additives in aqueous lubricants [6, 123, 124]. Phosphate IL tribochemical reactions can induce ultralow friction, even superlubricity when used as an aqueous lubricant on ceramic surfaces [6, 123, 124]. The molecular study revealed that under shear, the phosphate could form polyphosphate, which connects with contacting surfaces through a water layer [16]. This water layer separated the polyphosphate trilayer and the contacting surfaces while lubricating the interface (Fig. 10). A similar effect can also be found

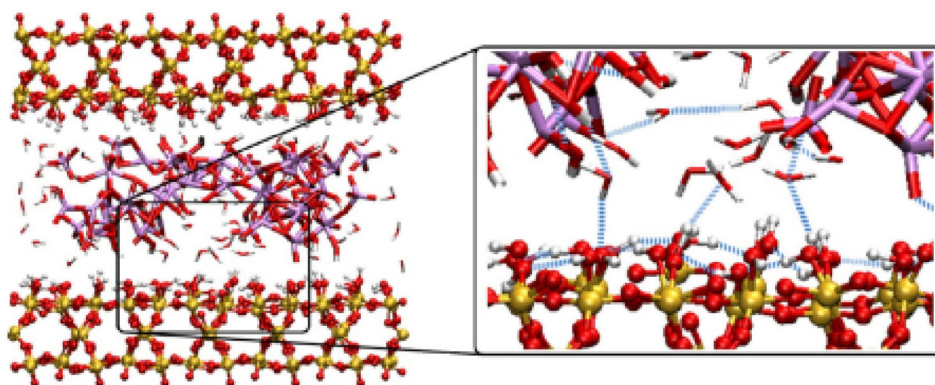


Fig. 10 Water molecules separate the tribochemically formed polyphosphate layer and the silica in molecular dynamics simulation. Reproduced with permission from Ref. [16], © American Chemical Society 2013.



in phosphoric acid, along with boric acid-lubricated silica surfaces [7, 125].

The product of IL tribofilm reaction is closely related to the tribochemically active elements that it contains. Table 5 lists the commonly used IL lubricant additives and the properties of the formed tribofilms. The phosphorus-containing IL forms phosphate, sulfur-containing IL forms sulfide, and nitrogen-containing IL forms nitride. The tribochemical reactions of ILs further prove the importance of P and S elements in such reactions. Even though there are ILs

that do not contain P and S such as $[C_4C_1Pyrr][B(CN)_4]$, the Fe_2B tribofilm it forms has a high COF in the boundary lubrication regime and cannot effectively protect the surface from wear [117]. The lack of carbon in almost all IL tribofilms listed in Table 5 also indicates that the general rules for ILs' tribochemical decomposition exist. It is observed that the bond between the alkyl chain and charge center cleaves under tribological shear. This cleavage of bonds in imidazolium was observed by the IL gas emission spectrometry [126, 127].

Table 5 ILs and the resulting tribofilms.

IL	COF and boundary lubrication	Miscible with lubricating oil	Tribochemical product	Ref.
$[(C_{12}H_{25})_3NC_3H_6PO_3(C_2H_5)_2]^+$ [DOSS] ⁻	0.12	Miscible	Inorganic phosphates and nitrides	[112]
$[(C_{12}H_{25})_3NC_3H_6PO(OC_2H_5)_2]^+$ [CH ₃ (CH ₂) ₁₀ COO] ⁻	0.12	Miscible	Inorganic phosphates and nitrides	[112]
POPA	0.07	Miscible	Polyphosphate	[106]
PTPA	0.065	Miscible	Polyphosphate	[106]
1-ethyl-3-methylimidazolium diyanamide	0.2	Not miscible	Nitrides	[128]
1-ethyl-3-methylimidazolium tetracyanoborate	0.2	Not miscible	Nitrides	[128]
1-n-butyl-1-methylpyrrolidinium tetracyanoborate	0.2	Not miscible	Nitrides	[128]
[BMIM] [NTf ₂]	0.26	Not miscible	Nitrides	[126]
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	0.11	Not miscible	FeF ₂ and FeS	[114]
1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	0.12	Not miscible	FeF ₂ and FeS	[114]
Choline bis(2-ethylhexyl) phosphate	0.16	Miscible	FePO ₄ and FeS	[129]
Choline dibutyl dithiophosphate	0.16	Miscible	FePO ₄ , FeSO ₄ , and FeS	[129]
trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate	0.08	Miscible	Polyphosphate and FeS	[116, 130]
[P66614][DEHP]	0.1	Miscible	FePO ₄	[131]
Choline bis(2-ethylhexyl)-phosphate	0.09	Not miscible	Polyphosphate	[132]
Tetradecyl-trihexyl-phosphonium bis(2,4,4-trimethylpentyl)-phosphinate	0.1	Not miscible	Polyphosphate	[132]
Tetradecyl-trihexyl-phosphonium bis(trifluoromethylsulfonyl)-imide	0.1	Not miscible	Polyphosphate	[132]
Tetraoctylphosphonium bis(2-ethylhexyl)phosphate	0.1	Miscible	FePO ₄ and FeO _x	[133]
PAPN	0.06	Miscible	Iron phosphates	[134]
LAPN	0.08	Miscible	Iron phosphates	[134]
Tributylmethylphosphonium dimethylphosphate	Not reported	Miscible	Iron phosphates	[135]
1-ethyl-3-methylimidazolium trifluoromethanesulfonate	0.003 (Si ₃ N ₄ /SiO ₂)	—	Ammonia salts and sulfides	[136]
[C ₈ H ₁₇] ₃ NH·Tf ₂ N	0.07	Neat	Iron sulfides	[137]

3.4 NPs

NPs have been used as additives in lubricants to enhance their tribological performance [3, 138]. Stable dispersion has been achieved in nanolubricants [138]. Like other additives, the NPs can be adsorbed on the contacting surfaces. This adsorption is driven by the van der Waals interactions between the NPs and the surfaces [3, 139]. In some cases, the adsorption of NPs can directly reduce the friction in the boundary lubrication regime and protect the surfaces from contacting [140, 141]. However, with the tribochemical reactions, the NP additive can have better tribological performance.

For some NPs such as metal oxide NPs, there are no tribochemical “reactions” because the composition of the tribofilm they form has the same composition as the NPs. They are essentially sintered to the contacting surfaces by the tribological process [82, 142–148]. There is also a report on tribochemically active oxide NPs such as Fe_3O_4 . The metal elements can be reduced and/or oxidized via tribochemical reactions [71, 149]. This oxidation reaction promoted by the oxide NPs is essential to the chemical–mechanical polishing process [35, 150–153]. In these reactions, the NP tribochemical reactions chemically wears the surface instead of protecting it. The overbased detergents are NP lubricant additives that can effectively reduce wear by forming a tribofilm [12, 154]. This NP is also tribochemically inactive. The formation of its tribofilm is mechanical rather than chemical [12]. The capped metal NPs can reduce wear and friction without tribofilm formation [155]. In some cases such as copper NPs [156] and silver NPs [157], the tribofilm can form directly by mechanical cold welding. One exception to the capped metallic NPs is the dodecanethiol-modified palladium NPs. The dodecanethiol-capped palladium forms palladium sulfide on the contacted surface when used as a lubricant additive [158]. The rare earth-containing NPs can form iron oxide tribofilms through the oxidation-catalysis effect [159].

One of the most successful NP friction modifying additives, inorganic fullerene molybdenum disulfide (IF-MoS₂), has its friction modifying ability due to its tribochemical reactions. MoS₂ is known to be a

solid lubricant as a powder or additive [160]. Under tribological forces, IF-MoS₂ forms a tribofilm comprised of 2H-MoS₂ and chemically bonds to the iron oxide on the steel surface [161]. The mechanism of this reaction was proposed that the mechanical breakdown of IF-MoS₂ nanosheets can tribochemically bond to the iron/iron oxide [161]. The iron sulfide can also be found in the tribofilm formed by MoS₂ and WS₂ NPs [162, 163]. The MoO₃ NPs can tribochemically react with olefin polysulphide to form MoS₂ [164, 165]. The molecular dynamics simulation also shows that MoS₂ nanosheets were more stable between contacting surfaces compared to the amorphous phase (Fig. 11) [101].

The WS₂ tribochemical process creates a film with a layered structure. The top layer of WS₂ tribofilm is a mixture of WS₂, WO₃, and Fe oxides (Fig. 12) [166]. The bottom layer is comprised of the reduced W and Fe. Unlike oxide NPs, WS₂ can actively react with Fe and Fe oxides, forming oxides and even W metal. Here, the similar “surface concentration” phenomenon observed in MoDTC is found. The formed metal disulfide seemingly gravitates towards the contacting surface.

The surface-adsorbed NPs, when mechanically broken by the tribological processes, can produce some active materials due to the resultant high surface area. This can explain why the sulfur or phosphorus-containing NPs, while having low hardness, can greatly improve the boundary lubrication performance of a lubricant [3]. The nanosheet of MoS₂ can readily react with iron and iron oxide [161].

Similar to ZDDP and ILs, different elements act differently in NP tribochemical reactions. When the NPs contain nitrogen or phosphorus, the product of the tribochemical reaction is mainly nitrides and phosphides [167, 168]. Similarly, CaF₂ NP and ZnB NP form FeF₂ and Fe₂B when tribochemically reacting with a steel substrate [169, 170]. The α -ZrP NPs, which contain phosphorus, form iron phosphate, which protects the surface from wear [171–173]. Carbon in NPs stays tribochemically inactive to metal surfaces. When graphene quantum dots were used as an additive, they tribochemically formed a fullerene structure instead of reacting with the contacting surfaces [174]. The CaCO₃ formed a tribofilm comprised of CaCO₃ and

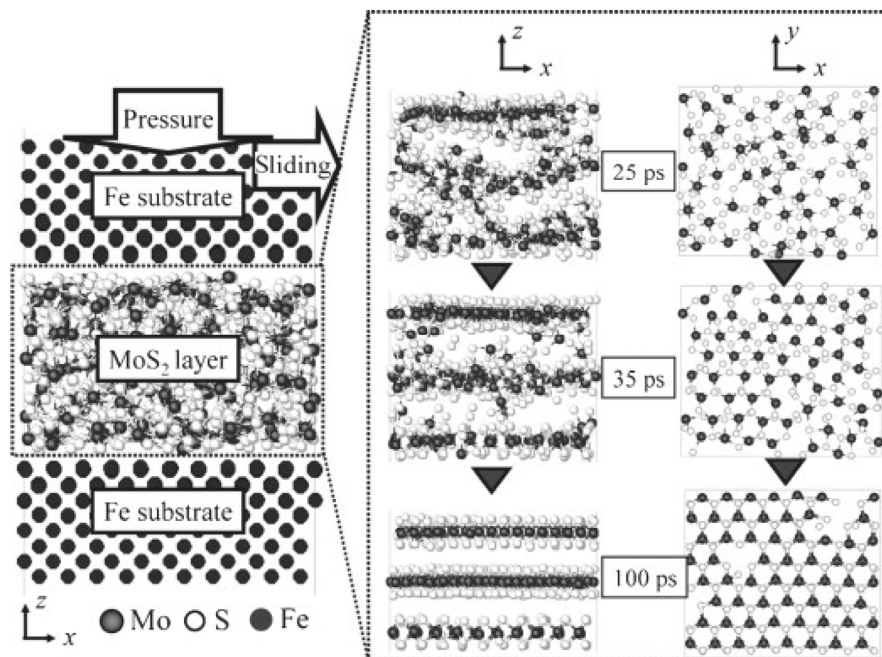


Fig. 11 Simulated tribochemical reaction of MoS_2 . It shows that the MoS_2 NPs can form 2D MoS_2 under shear force. Reproduced with permission from Ref. [101], © Elsevier B.V. 2008.

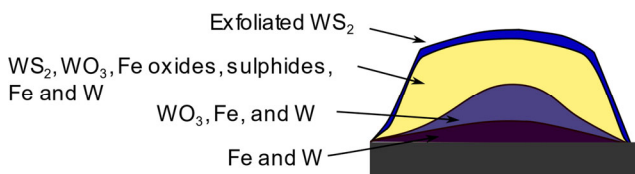


Fig. 12 Cross-section image of tribofilm formed by WS_2 NPs. Reproduced with permission from Ref. [166], © Springer Science+Business Media New York 2013.

CaO , and the carbon was removed from the NPs during the tribochemical process [175]. Interestingly, the DDP-coated ZnS NPs tribochemically formed a film similar to ZDDP [176].

With a proper catalyst, the normally tribochemically inactive carbon can tribochemically form carbon nanostructures. Carbon-based NPs under tribological force can form a glass phase with an amorphization process when mixed with iron NPs [177]. The tribological forces also reduced the Gibbs free energy of structurally more complex phases. This led to a phase transformation from the amorphized phase to onion-like carbon [177, 178] or carbon nanotubes [179]. This process started with reactions between iron NP and graphite [177], which formed an amorphous carbon-containing iron carbide. The amorphous phase under tribological forces then transformed into onion-like

carbon with superior tribological properties. It appears that the reason behind the inactivity of the alkyl chain in all the lubricant additives is caused by the strong carbon–carbon bond. The addition of iron disrupted this bond and made carbon tribochemically active.

3.5 Interactions between additives

It is known that the formulation of lubricants usually contains more than one additive. The tribochemically active additives sometimes display a “synergistic” effect. Most prominently, the ZDDP has been found to have such effect with MoDTC, IL, and NPs.

Adding MoDTC into the lubricant oil containing ZDDP would increase its friction reduction ability but harm its anti-wear effect slightly [180, 181]. The zinc ion in ZDDP increased the reactivity of MoDTC while enhancing the friction reduction [182].

The lubricant containing both phosphonium-alkylphosphate IL and ZDDP has an improved anti-wear and friction reduction performance than that only contains one additive [183]. Other studies on different ILs and ZDDPs were observed with similar effect [184, 185]. The synergistic/antagonistic effect between ZDDP and IL is related to the anion exchange of ZDDP [183], which could change the sulfur content

of the tribofilm [185]. However, the synergy between IL and ZDDP is not guaranteed, and the ILs can have no synergy effect or even antagonistic one with ZDDP [185, 186].

Adding NPs to ZDDP- or MoDTC-formulated oil can improve its performance. The calcium carbonate NPs can strengthen the tribofilm by incorporating ZDDP and MoDTC [187, 188]. The presence of ZDDP can also improve the anti-wear and friction-reduction behavior of WS₂ NPs [189, 190].

4 Summary and prospects

The tribochemical process is essential to the lubricant additive functions, especially its anti-wear and friction modifying properties. This work reviewed the kinetics of the tribochemical processes involving lubricant additives with elements in metallic substrates. Focusing on additives, we discussed organic phosphates', ILs', and NPs' tribochemical reactions and concluded as follows.

1) The occurrence of the tribochemical reactions requires chemical or physical adsorption of lubricant additive to the contacting surfaces.

2) Phosphorus, sulfur, fluorine, and nitrogen are active in those reactions. They can react with the metal surface regardless of the additive type.

3) Most reaction products are amorphous in nature. The only exception is transitional metal sulfide. This forms a 2D nanosheet, which gravitates to the contacting surface.

4) The ZDDP and MoDTC can thermally be decomposed under elevated temperatures, while IL and NP additives are thermodynamically stable.

5) A tribochemical reaction is thermodynamically controlled by a force applied to the additive covalent bond. Such a force changes the free energy of the reactant and the product.

6) The kinetics of tribochemical reactions are affected by the temperature, shear stress, and the wear of the tribofilm.

Among the literature collected, the majority reports were about ZDDP and MoDTC additives. Those about ILs and NPs have been focused on various additives. Comprehensive understanding in tribochemical reactions is expected to be obtained in close future.

Furthermore, it remains to be a challenge to find a “green” lubricant additive, which has favorable performance due to the essentiality of the phosphorus and sulfur in tribochemical reactions. The metal nitride, which has good performance as a coating, is unable to outperform phosphate or sulfide as a tribofilm. A low friction tribofilm generated from protic ILs may lead to a phosphor- and sulfur-free lubricant. Under vacuum, the graphene, which is normally inactive in a tribochemical process, forms inorganic fullerene when iron oxide is used as a catalyst. Finding an equivalent tribochemical process in lubricating oil may help the development of effective “green” lubricants.

Achieving superlubricity with tribochemical reactions has attracted attention in recent decades. The tribochemically formed polyphosphate under aqueous solution and onion-like carbon under dry nitrogen both displayed superlubricity. If those reactions can be replicated under non-polar lubricant, the performance of lubricant under mixed and boundary lubrication regime can be greatly enhanced.

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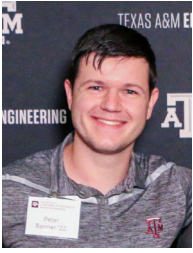
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