# Interpretation of experiments on ZDDP anti-wear films through pressure-induced cross-linking

N.J. Mosey [a], T.K. Woo [a,b,*], M. Kasrai [a], P.R. Norton [a], G.M. Bancroft [a], and M.H. Müser [c,**]

[a] *Department of Chemistry, University of Western Ontario, London, Ontario, Canada, N6A 5B7*
[b] *Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5*
[c] *Department of Applied Mathematics, University of Western Ontario, London, Ontario, Canada, N6A 5B7*

We review a recently developed molecular-level theory for the formation and functionality of zinc dialkyldithiophosphate anti-wear films [N. J. Mosey, M. H. Müser and T. K. Woo, Science 307 (2005) 1612]. This theory is based on the idea that pressure-induced cross-linking leads to chemically connected networks. The formation of cross-links modifies the mechanical properties of the films such that wear inhibition may be enhanced. Furthermore, the networks remain intact upon release of the pressure, which resists flow of the film out of the contact area. The ability of the theory to account for a diverse body of experimental data related to anti-wear additives and films is discussed. Routes towards the development of new AW additives are also suggested on the basis of the theory.

**Keywords:** zinc dialkyldithiophosphates, anti-wear films, ab initio molecular dynamics

## 1. Introduction

Seventy years after their development, zinc dialkyldithiophosphates (ZDDPs) remain key anti-wear (AW) additives in commercial lubricants used in automotive applications [1,2]. This is particularly remarkable considering that significant efforts have been made over the last decade to replace ZDDP in engine oils. The rational design of new AW additives has been hindered by the absence of a basic understanding of the functionality of ZDDP. In fact, until very recently no single theory existed that could convincingly explain the abundance of experimental observations regarding these additives. Relevant phenomena include the dependence of the AW capabilities of ZDDP upon the nature of the surface material, the effects of other lubricant additives on wear inhibition and the differences between films formed under thermal and rubbing conditions.

It is well-established that ZDDPs do not inhibit wear directly, but rather decompose at high temperatures and/or with rubbing to form protective zinc phosphate (ZP) films [3–5]. Generally, it is agreed that decomposition occurs through a series of thermo-oxidative reactions [6], which yield various precursors to the AW films. Existing theories of film formation are based on complex reaction schemes in which the surface catalyzes the formation and/or polymerization of these precursors to promote film growth [5,7]. As a result, one would expect the formation and behavior of these films to be dictated by the *chemical* properties of the underlying substrate. The similarities between ZDDP AW films formed on a number of chemically distinct surfaces suggests otherwise [8–12].

Recently, an alternative theory for the formation and functionality of ZDDP AW films has been developed through first-principles molecular dynamics simulations of ZPs [13]. This theory is based on the notion that pressure induces the formation of cross-links through the zinc atoms within ZP systems. Cross-linking transforms a viscoelastic fluid of loosely interacting ZP molecules into a chemically connected network with zinc atoms acting as network forming agents. Network formation occurs only if a certain threshold pressure is exceeded. Otherwise, the system remains in a disconnected state. Thus, the theory indicates that AW film formation is dictated primarily by the *mechanical* properties of the underlying surface, which limit the maximum pressures to which the ZP system is exposed.

Perhaps more importantly, the new theory sheds light on the atomic-level details of ZDDP AW films that

---

[*] Email: twoo@uottawa.ca
[**] Email: mmuser@uwo.ca

are responsible for wear inhibition. Essentially, cross-link formation strengthens the film, redistributing the pressures to which an underlying surface is exposed. The ability of the film to inhibit wear is limited by the mechanical properties of the substrate, which must allow the system to attain pressures sufficiently high to induce cross-linking, while remaining harder than the cross-linked film. This theory provides a molecular-level picture of the relevant processes that is consistent with the interpretation of experiments reported recently in which a relationship between the efficacy of ZDDP AW films and the yield strength of the substrate was proposed [9]. Otherwise, the insight into the functionality of ZDDPs offered by the simulations differs drastically from conventional theories, which consider the films to be sacrificial boundaries composed of easily sheared layers [14], which may digest third-body abrasives [15] and prevent corrosive wear [16,17].

The strength of the new theory lies in its interpretive and predictive capabilties, which are limited in existing models. In this letter, we demonstrate these abilities by interpreting a myriad of experimental observations related to ZDDPs. In section 2, we review the pressure-induced theory of ZDDP AW film formation and functionality in greater detail. In section 3, a comparison is drawn between experimental observations reported previously regarding ZDDPs and the predictions derived from the theory. Routes towards the development of new AW additives based on the notion of pressure-induced cross-linking are outlined in section 4. The conclusions are summarized in section 5.

## 2. Summary of the Theory

In this section, the cross-linking theory for the formation and functionality of ZDDP AW films is reviewed briefly. The simulations upon which the theory is based are explored first. The results of these simulations are then considered within the context of how ZDDP AW films are formed and inhibit wear.

### *2.1. Compression of zinc phosphates*

ZDDP AW films are formed and function at regions exposed to the highest loads during sliding, such as the points where asperities come into contact. Thus, to develop a theory of ZDDP AW films, it is necessary to understand the behavior of ZPs in response to the conditions encountered during asperity collision. These conditions include pressures, $p$, and temperatures that exceed the theoretical yield strength, $p_y$, and melting point of the substrate, respectively [18]. The films are exposed to these conditions on the brief time scales at which asperity contact occurs. Molecular dynamics simulations based on first principles quantum chemical calculations were performed to examine the behavior of ZPs under these extreme conditions. The results of these simulations are examined briefly in what follows.

The simulations upon which the theory is based have been described elsewhere [13,19]. Here, we describe only the details that are necessary to understand the cross-linking theory. The systems considered were composed of small (zinc) phosphate molecules that were initially aligned randomly within simulation cells that were repeated periodically in three dimensions. Several different systems were considered, with either one or two zinc atoms per simulation cell and the ratio of phosphorus to zinc set between 2:1 and 5:1. The molecular systems were briefly exposed to temperatures of up to 1000 K. This initial equilibration period reoriented the molecules within the simulation cell and, in some cases, resulted in the formation of longer linear ZPs. The formation of such species is consistent with experimental results indicating that ZDDP is transformed into phosphates of various chain lengths prior to film formation [6,20].

Following the initial equilibration procedure, the systems were exposed to isotropic pressures that were varied linearly at a rate of 10.0 GPa/ps from an initial value of 0.25 GPa to maximum values, $p_{\max}$, between 2.5 and 32.5 GPa. Once $p_{\max}$ was reached, the pressure was decreased to 0.25 GPa at the same rate. This procedure, which we refer to as a c/d cycle, is intended to mimic the conditions encountered during asperity collisions, where the film is exposed to rapid increases and decreases in pressure. However, we recognize that the time scales considered here are two to three orders of magnitude shorter than those on which asperity collision occurs. Unfortunately, it was not possible to use a slower compression rate due to the significant computational expense of these calculations. Simulations showed that decreasing the rate to 2.5 GPa/ps did not significantly affect the pressures at which the relevant chemical processes occurred and we believe that processes consistent with those reported here take place in

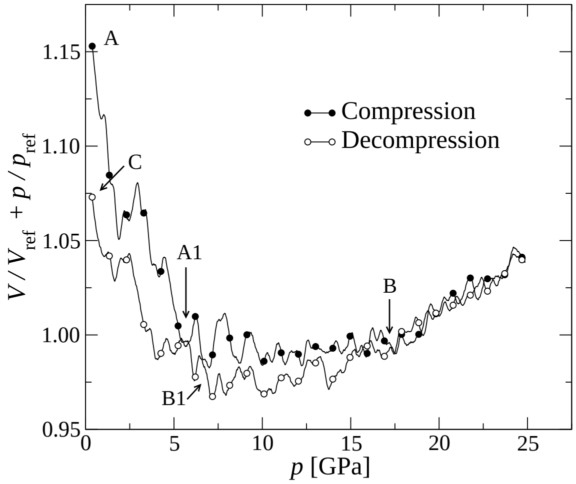

Figure 1. Instantaneous normalized volume, $V/V_{\mathrm{ref}} + p/p_{\mathrm{ref}}$ as a function of pressure, $p$, for the zinc phosphates. $V_{\mathrm{ref}} = 200$ cm$^3$/mol and $p_{\mathrm{ref}} = 80$ GPa. Key points along the plot are denoted with the labels A through C and are discussed in the main text. The representation of the data as $V/V_{\mathrm{ref}} + p/p_{\mathrm{ref}}$ against $p$, instead of $V$ against $p$, was performed to keep the plotted data in a narrow range. The bulk modulus, $B$, can be approximated in units of GPa as $B =$ (-local slope + 1/80)$^{-1}$.

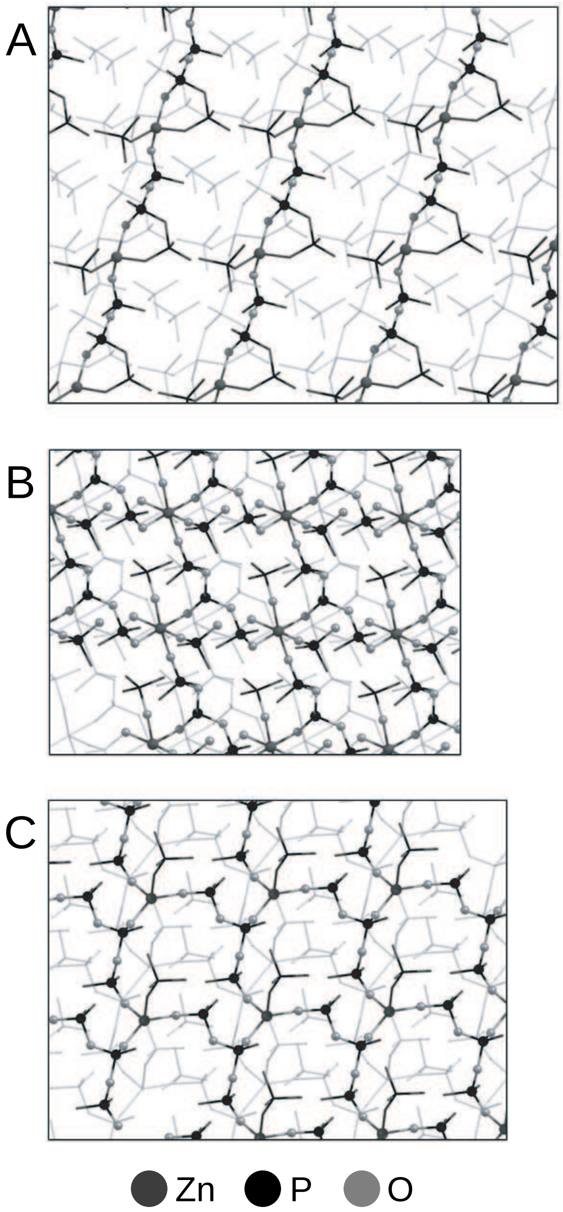

Figure 2. Representative structures of the system observed during the simulation. **(A)** The initial structure. **(B)** The structure with hexacoordinate Zn observed above 17 GPa. **(C)** The final structure of the c/d cycle. In all cases the simulation cell is shown repeated periodically. Atoms involved in extended bonding are denoted with a ball-and-stick representation. Atoms in underlying layers are faded out to aid in visualization. Hydrogen atoms have been omitted for clarity.

real systems as long as the film is compressed sufficiently fast to prevent flow out of the contact area.

The $p_{\mathrm{max}}$ values used in the simulations span pressures accessible on various materials of interest, including iron ($p_{\mathrm{y}} \sim 21$ GPa) and aluminum ($p_{\mathrm{y}} \sim 7$ GPa). This will provide insight into the behavior of ZPs on these substrates. Temperatures spanning 100 K to 1000 K were considered and found to have little effect on the results; again indicating a weak dependence on the compression rate. Moreover, the results are not affected significantly by the initial structure or composition of the system, provided that zinc is present.

The calculated equation of state for a system with the chemical composition $\mathrm{ZnP_5O_{18}H_9}$ and $p_{\mathrm{max}} = 25.0$ GPa is shown in Fig. 1. At the start of the simulation, point A in Fig. 1, the system was composed of linear ZP chains with tetracoordinate zinc atoms. This structure is shown in Fig. 2A and was obtained by compressing and decompressing a molecular ZP system in an earlier simulation as described above. At ~6 GPa, point A1 in Fig. 1, the zinc atom changed from a tetrahedral to a 'see-saw' geometry, which allowed this atom to interact with neighboring oxygens. This led to the formation of new Zn-O bonds, at the expense of those present initially. Overall, this behavior altered the specific arrangement of bonds at zinc. The effects of this transformation are discussed later. The transition to the see-saw geometry also increased the bulk modulus of the system to ~80 GPa.

When the applied pressure reached ~17 GPa, point B in Fig. 1, the zinc atom adopted a hexacoordinate bonding arrangement through the formation of two additional Zn-O bonds. This process transformed the system into a fully connected ZP network, with extended bonding in all three spatial directions from zinc. A typical structure of the system observed above 17 GPa is shown in Fig. 2B. The formation of the highly cross-linked network increased the bulk modulus of the system to ∼140 GPa. Increasing the pressure to $p_{\max}$ from this point did not alter the connectivity of the system further.

During decompression from $p_{\max}$ the zinc atom reverted to a tetracoordinate state at 7 GPa, point B1 in Fig. 1. When fully decompressed, point C in Fig. 1, the system exhibited the structure shown in Fig. 2C. Comparison of the two low-pressure structures, Figs. 2A and 2C, shows that the net result of the c/d cycle is the transformation of linear ZP chains into ZP sheets. The terms chains and sheets should not be taken too literally in light of the small systems considered, however, it is clear that cross-linking occurred, which increased the internal connectivity and bulk modulus of the system at low pressure.

### *2.2. Formation of ZDDP AW films*

At the start of the simulation the system was composed of loosely-interacting ZP chains, which are analogous to those formed through the decomposition of ZDDP. The final, decompressed state corresponds to a moderately connected ZP network, which is consistent with the AW film. As noted above, the transformation between these two states occurs through the irreversible pressure-induced formation of cross-links at the zinc atoms, which we suggest is responsible for film formation. The zinc atom is tetracoordinate in each of the low pressure structures, however, the specific arrangement of bonds at this atom has changed. This is facilitated by the formation and dissociation of Zn-O bonds when the zinc atom adopted a see-saw geometry during compression. Multiple simulations showed that this process occurred as long as the system was exposed to pressures greater than ∼5 GPa. Irreversible cross-link formation was not observed during simulations of pure phosphates [19], which demonstrates the importance of cations in the cross-linking process.

### *2.3. Functionality of ZDDP AW films*

ZDDPs are effective wear inhibitors on hard materials, such as iron, which has $p_{\mathrm{y}} \approx 21$ GPa. This exceeds the pressure necessary to induce the reversible transition to hexacoordinate Zn atoms within the ZPs, which occurs at ∼17 GPa. The transition to hexacoordinate zinc increases the cross-link density and bulk modulus of the film, $B_{\mathrm{film}}$, to ∼140 GPa. The increased stiffness of the film improves its capacity to accommodate and redistribute applied loads, which reduces wear of an underlying surface. Additionally, the film remains softer than the iron substrate ($B_{\mathrm{iron}} \approx 170$ GPa), which prevents it from abrading the surface. Thus, it is anticipated that ZDDP AW films will be most effective on surfaces where $p_{\mathrm{y}}$ is greater than approximately 17 GPa and where $B_{\mathrm{surface}} > B_{\mathrm{film}}$. These criteria are satisfied by iron and, hence, we propose that the impressive AW capabilities of ZDDPs on steel and cast iron are due to the pressure-induced transition to the highly cross-linked state. Here, and in what follows, we have assumed that an increased stiffness corresponds to an increased hardness, which is true, in general, for many non-metallic materials [21–23]. However, we recognize that such a relationship does not necessarily hold in all cases.

## 3. Comparison to Experiment

In this section, the results of several experimental studies of ZDDP additives and films are interpreted within the context of the theory presented in the preceding section. The experimental results considered encompass a wide variety of phenomena including the formation, mechanical properties and chemical composition of the films, the performance of ZDDPs on different substrates and the effect of other lubricant additives on the efficacy of ZDDPs.

Before proceeding, it is important to note that wear regimes may exist in which the mechanisms described above do not apply. In fact, experiments have been reported in which very low wear rates were observed despite minimal film formation [24]. Although we do not wish to speculate on the origins of these observations, it seems clear that the low wear rates in those experiments are not due to the presence of AW films. The case of very low loads may be an additional example where the importance of AW films may not be significant. In the low-load regime, it is unlikely that hard AW films would form through the mechanisms described above. Therefore, this theory does not apply to that regime.

### *3.1. Decomposition of ZDDP*

As mentioned above, ZDDPs decompose under engine conditions to form protective ZP films. It is generally agreed that decomposition occurs through thermooxidative reactions that remove alkyl groups and sulfur atoms from ZDDP [6]. These processes yield ZP molecules, which contain Zn, P and O in higher concentrations than the original additive and are precursors to the AW films. The decomposition byproducts observed experimentally include olefins and sulfides [25,26]. Numerous reaction schemes have been developed to account for the transformation of ZDDPs into ZPs through the elimination of these species. Such schemes are based on hydrogen or alkyl group transfer [5,20,25–27], as well as the elimination of alkyl radicals [28]. These processes are thought to be responsible for the induction period incurred prior to film formation, which is consistent with the dependence of the rate of formation on the temperature of the oil [20,29] and the nature of the alkyl substituent on the ZDDP molecule [25,27].

The simulations described in section 2 were performed on ZPs and, hence, the theory itself cannot account for decomposition of ZDDP. Nonetheless, it is important to understand the decomposition processes in order to justify the model system used in the calculations and gain fundamental insight into processes that occur during the initial stages of film formation. This has been the focus of previous simulations [30–33]. In those studies, several decomposition routes accessible to ZDDPs were identified and explored at the molecular level. It was found that the elimination of olefins and $H_2S$ can occur through intramolecular $\beta$-hydrogen transfer [33], while dialkyl sulfides can be formed through alkyl group transfer [32]. The previous simulations also suggest that linkage isomers of ZDDPs may decompose through the elimination of metathiophosphates [31]. In general, these reactions remove the alkyl groups and a significant proportion of the sulfur atoms from ZDDP in a manner consistent that is with experimental results [25–27]. More recent simulations have shown that the decomposition products can react with one another to yield ZP chains [30], which is consistent with experimental results indicating that ZDDPs are transformed into longer phosphates prior to film formation [20]. Overall, these results suggest that ZDDP decomposes thermally along reaction pathways that lead to the formation of ZPs such as those considered in the calculations discussed in section 2.

### *3.2. Formation of AW films*

The transformation of the ZP decomposition products into ZP films can occur in either of two ways [5]. Under purely thermal conditions, i.e. without rubbing, the ZPs collect on surfaces to slowly form ‘thermal films’, which are composed of ZPs distributed rather evenly across the surface. Under sliding conditions, however, the ZPs are transformed rapidly into ‘AW films’, which are much harder than those formed thermally. The formation of AW films is intiated preferentially at locations exposed to the highest loads during sliding, such as the tops of asperities [11,20,34–37] and, hence, these films exhibit a patchy morphology. For example, in a recent study it was reported that a ZP film approximately 10 nm in height was formed after only 10 seconds of rubbing followed by the appearance of isolated ZP ‘islands’ with 30 seconds of rubbing [38]. The mechanism through which the ZPs are transformed into AW films is poorly understood, however, it must proceed more quickly than the rate-limiting thermooxidative decomposition processes to account for the overall rate of film formation.

The pressure-induced theory described in section 2 leads to a description of film formation that is consistent with the extremely rapid rate of film formation. Cross-linking occurs only if the system is exposed to sufficiently high pressures, resulting in the preferential formation of films at load-bearing points. The incorporation of ZP precursors into the AW film through cross-linking occurs at the sliding rate, which is much faster than that of ZDDP decomposition. Hence, if ZP precursor molecules are not present, such as in the initial stages of rubbing fresh oil, the period of time before films are formed will depend primarily upon decomposition of ZDDP. Finally, the high degree of cross-linking within the film improves its ability to resist shear under sliding conditions, allowing for the rapid growth of intact ZP pads. Thus, the growth process derived from the theory outlined in section 2 predicts that isolated ZP pads are formed at load-bearing points on short time scales, as observed experimentally [38].

### *3.3. Film formation on aluminum alloys*

The experiments considered in the previous section dealt primarily with the formation of ZDDP films on iron-based substrates such as steel and cast iron, which are the basis of most engines. Recently, interest has arisen in the development of aluminum engines as a means of decreasing vehicle weight, which improves fuel economy. This interest has prompted research into the behavior of ZDDPs on aluminum alloys [8–10,39,40]. In general, the substrates considered in those studies contained various amounts of silicon, which is used to strengthen the alloy. On substrates with a high silicon content, raised silicon grains protrude from the aluminum matrix and act as the load-bearing surfaces. Naturally, aluminum supports the load when the silicon content is low. It is likely that the aluminum surface is covered initially with a thin layer of $Al_2O_3$, however, it has been suggested that this layer is removed during the early stages of rubbing to expose the nascent metal, which is soft [8]. It has been found that film formation occurs regardless of the silicon content of the alloy, however, on substrates with a high percentage of silicon, films form preferentially on the raised silicon grains [8]. Films formed on aluminum and silicon both exhibit mechanical and chemical properties that are virtually identical to those those of films formed on steel [8,10].

The pressure-induced mechanism described in section 2 indicates that AW film formation should occur as long as $p_\mathrm{y}$ of the substrate is greater than 5 GPa and the temperature of the system is high enough for ZDDP to decompose into ZPs. The theoretical yield strengths of aluminum ($\sim$ 7 GPa) and silicon ($\sim$ 10 GPa) are both in excess of that required to intiate cross-linking and film formation (5 GPa). Thus, the theory predicts that films should form on aluminum, silicon and steel, which is the case. It has suggested that the similarities between films found on the silicon grains and on the aluminum matrix is due to film transfer from the former to the latter [8]. The preferential formation of films on the raised silicon islands, which is observed experimentally and necessary for such a scenario to take place, is also consistent with pressure-induced cross-linking since the tops of these islands will be exposed to the highest pressures during sliding.

### *3.4. Chemical composition of AW films*

ZDDP AW films are composed of thick ZP pads ~200 to 400 nm in height separated by valleys, which contain a thinner layer of ZPs. Spectroscopic studies show that differences exist in the chemical properties of films at these two locations [41,42]. Spectra recorded at the tops of the pads are reminiscent of ZPs with chain lengths that are longer than those found in the valleys. Such conclusions are made by comparing the recorded spectra with those of known phosphate compounds. It is important to note, however, that this approach does not allow for the characterization of the specific chemical connectivity within the film.

The mechanism described in section 2 predicts that the high pressures attained at the tops of the asperities induce the greatest degree of cross-linking, which in turn, is manifested in spectra as an apparent increase in chain length. On the other hand, significantly lower pressures are achieved in the valleys, which leads to minimal cross-linking and spectra indicative of shorter ZP chains.

### *3.5. Mechanical properties AW films*

The mechanical properties of the AW films play an important role in wear inhibition. Nanoindentation studies show that the films are stiffest at the top of the AW pads, less stiff at the edges and softest in the valleys. [35,43–48]. Recently, spectroscopic methods and nanoindentation techniques have been used in tandem to determine the chemical and mechanical properties at the same specific points on the film [41]. The results of that work clearly showed that the 'longest' ZP chains are found at regions where the film is stiffest, such as the tops of the pads, while shorter ZPs were located in the valleys where the film is softer. These results demonstrate that the mechanical properties of the film depend sensitively upon the chemical structure of the ZPs.

The results of the simulations described in section 2 demonstrate that the bulk modulus of the ZP system increases with the cross-link density. As discussed in section 3.4, the highest degree of cross-linking occurs at the tops of the pads, where the ZPs are exposed to the highest pressures. Hence, the theory predicts that the film will be stiffest in these regions. Conversely, minimal cross-linking occurs in the valleys, which results in a significantly lower indentation modulus. The edges of the pads correspond to a region that experiences pressures between those encountered at the tops of the pads and those experienced in the valleys. Thus, moderate cross-linking will occur at these locations and the resulting film will exhibit an indentation modulus greater than that in the valleys, but less than that at the center of the pad. Taken together, these interpretations account for the measured variation in mechanical properties and, moreover, relate these properties to the chemical composition of the films in a manner that is consistent with experiment [41].

### *3.6. Response of films to applied loads*

ZDDP AW films have been observed to undergo a pressure-induced hardening *during* indentation [48]. The authors of that study described this as a complex process that allowed the film to accommodate the pressures applied during sliding, contributing to its capacity to inhibit wear. On the basis of this peculiar property, the films were described as 'smart' materials, which become harder to protect surfaces from high loads encountered under contact conditions.

The mechanism described in section 2 provides a plausible explanation for the observed hardening. In fact, the theory partially attributes the AW functionality of the films to their ability to become harder in response to applied pressure. The simulations show that the coordination at the zinc atoms is altered with pressure, yielding a stiffer film as the external pressure is increased. These chemical changes, and the associated hardening, which we assume is correlated with the increased stiffness, occur abruptly as the pressure thresholds necessary to induce changes in the coordination of Zn are surpassed. Consequently, the hardening of the film does not vary smoothly with the applied pressure. This most likely contributed to the inability of the authors of the experimental study [48] to develop a relationship between the applied load and the hardness of the film.

### *3.7. Dependence of wear on surface hardness*

The ability of ZDDP films to deter wear depends on the hardness of the substrate. In one study, wear tests were performed on a set of steel surfaces that were tempered to varying degrees, modifying their hardness [49]. Tempering does not alter the chemical composition significantly of the surface nor does it greatly affect the flash temperatures attained during rubbing. However, the maximum load that can be supported by the surface and, hence $p_{\mathrm{max}}$, increases with the hardness of the substrate. The tests showed that in the presence of ZDDP AW films, the wear scar width decreased abruptly to a relatively constant value as the hardness of the substrate increased. On the softer substrates, substantial wear occurred and the pads were smeared in the sliding direction. Analogous observations have been reported in studies of ZDDPs on aluminum alloys [9,10,39], which are significantly softer than steel, where it was found that substantial wear of the substrate occurred with rubbing. Examination of wear scars on aluminum alloys indicated that the film abrades and becomes embedded into the substrate.

In section 2, it was shown that the zinc atoms become hexacoordinate above pressures of approximately 17 GPa. The associated increase in cross-link density strengthens the film and improves its ability to inhibit wear. Furthermore, the simulations showed that once the zinc atoms adopt the hexacoordinate state, the chemical and mechanical properties of the film are not altered further with increasing pressure. Hence, the wear rate should be relatively unaffected once the hardness of the surface exceeds a certain value. On the softened steel samples it is likely that $p_{\mathrm{y}}$ is less than 17 GPa, yet above the 5 GPa necessary for film formation, and, hence, the zinc atoms cannot adopt the hexacoordinate state. This reduces the capacity of the film to both inhibit wear and resist shear, leading to smeared pads and higher wear rates. On the aluminum alloys we propose that the high degree of wear arises from a different origin altogether. The simulations showed that once the film is exposed to pressures greater than 5 GPa its bulk modulus increases to approximately 80 GPa. This is similar to, or even greater than, the bulk modulus of typical aluminum alloys ($\sim$ 70 GPa) and, hence, a hard film resides on a softer surface. Under the high loads experienced during sliding, this results in abrasion of the substrate and may cause the film to embed into the aluminum. Taken together, these facets of the cross-linking theory account for the differences in the nature of the film and wear scars on various surfaces of different hardness.

The discussion of the abrasion of aluminum surfaces was based on the notion that the AW film resides upon an aluminum metal substrate. In actuality, the surface is most likely covered with a thin film of aluminum oxide, which is signficantly harder than both aluminum and the AW film. However, experiments show that the aluminum oxide layer is only a few nanometers thick [9]. The aluminum substrate is too soft to support such a thin oxide layer under sliding conditions, which will lead to fracture of this layer thereby exposing the nascent aluminum surface as suggested previously [8]. The wear debris formed through this process will also act as an abrasive and uncover the aluminum substrate further. These processes will occur primarily during the initial run-in stage of rubbing and, hence, the nascent aluminum will be exposed when film formation occurs at a later point in time. This probably favors the wear scenario described above.

### *3.8. Effect of detergents*

Fully formulated engine oils contain additives other than ZDDPs, such as detergents, dispersants and friction modifiers. It is imperative to understand the effect of these additives on the efficacy of ZDDP. Dispersants alter the solution chemisty of ZDDPs [50,51], while friction modifiers have little effect on the AW properties of the films [52]. Detergents, on the other hand, alter the chemical composition of the films, affecting AW performance [45,53,54]. Common detergents contain calcium ions, which are incorporated into the ZP film by replacing Zn. On iron-based materials, this increases wear compared to that observed when ZDDP is used alone [45,53].

Calcium does not have a variable coordination number and, hence, cannot take part in the cross-linking processes described in section 2. This decreases the overall cross-link density of the film, reducing its bulk modulus and ability to redistribute applied loads. On iron surfaces, this causes the substrate to experience higher pressures and increases wear as observed experimentally. A positive aspect of this behavior is that softening the film through the incorporation of cations, such as calcium, may reduce abrasion of softer substrates, such as aluminum. The potential application of this concept towards the design of AW additives for use on soft materials is discussed in section 4.

### *3.9. Zinc-free additives*

Environmental concerns associated with the presence of zinc in engine oils has prompted research into the development of zinc-free (ZF) AW additives. Typical ZF additives are phosphorus-based species that are similar to the dithiophosphate ligands present in ZDDP [38,55–57]. In general, it is found that AW films are formed from both additives, however, ZDDP AW films offer greater protection, particularly for short rubbing times [38]. This may be due to the fact that ZDDP films are formed much faster than those derived from ZF additives. Chemical characterization of films formed in wear tests with ZF additives has shown that iron and zinc are distributed throughout the film [55,56]. In films derived from ZDDP, zinc is the main cation in the uppermost portion of the film, with the concentration of iron increasing towards the substrate.

The theory described in section 2 is based on changes in the chemical and mechanical properties of the ZPs due to changes in the coordination at zinc. It is highly probable that other elements with variable coordination numbers and geometries may be substituted for zinc while still allowing the relevant processes to occur. For systems without such elements, i.e. the phosphorus-based molecules examined as potential ZF additives, it is anticipated that wear will occur to a greater extent. In fact, additional simulations have shown that film formation will not occur if zinc is not present [19].

In the experiments mentioned above, the AW films derived from ZF additives contain high concentrations of iron, which exhibits variable coordination numbers and geometries. Presumably, the iron atoms are derived from the substrate and incorporated into the film through the formation and subsequent digestion of wear particles. Thus, this suggests that the formation of AW films from ZF additives requires wear of the surface to occur. This will lead to a longer period of time between the initiation of rubbing and higher wear rates with ZF additives than with ZDDP.

## 4. Rational Design of New AW Additives

The theory outlined in section 2 leads to basic requirements which must be satisfied by films that inhibit wear in a manner similar to ZDDP AW films. Simply put, an effective AW film will cross-link at pressures below $p_{\mathrm{y}}$ of the target substrate and remain slightly softer than the substrate. In this section, this concept is considered in conjunction with the results of the simulations of ZPs to suggest possible means of designing new AW additives and films. The following analysis focuses on the identification of key components in ZDDP AW films and suggests how these key components may be modified to develop new additives.

Before proceeding, we note that the theory in section 2 focuses solely on the behavior of ZPs derived from ZDDPs, particularly with respect to AW functionality. The models used in the simulations represent significant simplifications of the AW films and engine environment. As such, we cannot comment on the interactions of ZDDP molecules with other species present in the engine. Clearly such interactions are important, for example, in the role of ZDDPs as anti-oxidants. The engine environment will influence the efficacy of new AW additives significantly, however, considering such a complex system is beyond the scope of the simulations performed here. Additionally, the theory only provides an explanation at the nanometer scale. In its present version, it cannot be used to explain the significance of run-in and the experimentally-observed tribomechanical memory mechanism [58]. Such an endeavor would require coupling the first principles simulations to continuum-type models that span mesoscopic length scales. Thus, the suggestions presented in what follows should not be taken as strict rules that will definitely lead to effective new AW additives, but rather, these points should be considered as guidelines for use in the selection of promising candidate molecules with which to replace ZDDPs. Ultimately, experiments must be performed on such molecules to determine their behavior within an engine, which is far too difficult to model computationally. Nonetheless, the suggestions offered in what follows represent the first steps towards the rational design of new AW additives.

### *4.1. Cross-linking agents*

The theory described above is based on the notion that pressure-induced cross-linking is fundamental to both the formation and functionality of ZDDP AW films. In order for these processes to occur, effective AW films must contain elements that undergo pressure-induced changes in coordination number and geometry. We refer to these elements as cross-linking agents. Zinc plays this role in ZDDP AW films, however, many other elements undergo analogous pressure-induced changes in coordination. Thus, replacing zinc with a different cross-linking agent may be a relatively straightforward means of developing new AW additives. In fact, as noted in section 3.9, the incorporation of iron into phosphates formed from zinc-free additives also leads to the formation of AW films, however, these films do not protect iron surfaces from wear as well as those derived from ZDDP. To determine which elements would work best as cross-linking agents, it will be necessary to acquire information regarding the pressures at which different elements undergo changes in coordination.

### *4.2. Role of phosphorus*

One particularly interesting result of the simulations is that phosphorus is not involved directly in cross-linking. Clearly, the role of phosphorus as a glass former affects the basic structural and mechanical properties of the films, however, it may be possible to replace this element entirely within the film. Candidates with which to replace phosphorus include silicon and boron, which also form oxide glasses. Additionally, both boron and silicon exhibit variable coordination numbers, which may allow these elements to act as both glass formers and cross-linking agents. This would essentially eliminate zinc and phosphorus from engine oils, leading to more environmentally-friendly additives. Recently, the potential use of boron-based additives has been explored in several studies [59–61]. The results generally indicate that a borophosphate film is formed when these additives are used in conjunction with ZDDP. Wear tests show that the borophosphate films and the ZP films derived from ZDDP alone offer similar protection from wear and thus, such additives may be used in conjunction with ZDDP, leading to lower concentrations of zinc and phosphorus in oil. However, when the boron-based additives considered to date are used alone unacceptable wear rates occur and, hence, these particular additives are not suitable replacements for ZDDP.

### *4.3. Coordinating species*

Cross-linking occurs within ZPs through the formation of Zn-O bonds, which requires sufficiently high concentrations of oxygen. Clearly, oxygen is not the only element that can bond to zinc and, hence, other coordinating species may be used in AW films. This expands the scope of candidate AW films beyond oxide glasses, however, it will be necessary to consider the effect of such changes on the pressure-dependent properties of the films. That is, changing the coordinating species will alter the pressures at which cross-linking occurs and may alter the mechanical properties of the film significantly. These considerations must be taken into account when designing new AW additive systems.

### *4.4. New additive molecules*

The theory described above deals with the formation and function of AW films. This knowledge may lead to the identification of new AW films that meet modern technological and environmental requirements. Should this be achieved, it will be necessary to develop new additive molecules that can deliver the relevant components to the surface, where film formation occurs. In fact, this is the role played by ZDDP, which decomposes under engine conditions to form ZPs. Although the cross-linking theory does not account for the behavior of the additives, the details discussed in the preceding sections do point towards strategies with which to develop such molecules.

A potential strategy for the design of new AW additives may be the use of co-additives, which work in conjunction with ZDDPs and lead to modified ZP AW films. The calcium-based detergents discussed in section 3.8 and boron-based AW additives mentioned in section 4.2 are examples of co-additives. It may be possible to design molecules that contain various cross-linking agents and other components, which can be used in conjunction with ZDDPs to form AW films that cross-link at lower pressures and work on softer materials, such as aluminum. In terms of replacing zinc entirely, it will be useful to apply knowledge regarding the decomposition of ZDDPs. In section 3.1 processes were described whereby the ZDDP molecule decomposed through the elimination of alkyl groups and sulfur to form ZP precursors to the AW films. These principles could be used to design new additives, where the important components of the AW films are surrounded by superfluous functional groups that can be lost easily during the process of film formation.

## 5. Conclusions

We have reviewed a recently proposed theory for the formation and function of ZDDP AW films [13]. This theory is based on pressure-induced changes in the coordination of the zinc atoms in the ZP systems, which results in cross-link formation. This alters the chemical structure and mechanical properties of the film such that it may protect surfaces from wear. The degree of cross-linking within the film depends sensitively upon the maximum pressure to which it is exposed. The maximum applied pressure varies with the theoretical yield strength of the substrate and, hence, the theory provides a connection between the properties of the surface material and the behavior of the film.

The cross-linking theory was used to provide molecular level explanations for several experimental observations regarding ZDDPs that have been reported previously. Topics considered include the formation of films on iron and aluminum-based materials, the lateral heterogeneity in the chemical composition and mechanical properties of the films, the dependence of wear protection on the hardness of the substrate, the inability of ZDDPs to protect aluminum and the effect of detergents on the efficacy of ZDDPs on different materials. No single theory proposed previously has been able to account for such a breadth of experimental observations. We note the similarity between the interpretation of the simulations discussed here and the model proposed in a previous experimental study [9], where the efficacy of ZDDP was suggested to depend on the mechanical properties of the substrate. The results presented here, provide molecular-level insight into the underlying process that are responsible for this dependence, thus tying together the experimental and theoretical results nicely.

The basic details of the theory were used to identify key components of ZP AW films, which will aid in the development of new AW additives. The most important components in the films are cross-linking agents and species that coordinate to these cross-linking agents. In the ZP films considered here, these roles are played by zinc and oxygen, respectively. However, these properties are not unique to these elements and, hence, they may be replaced. Additionally, phosphorus does not play a direct role in the relevant processes, which may allow for the design of phosphorus-free additives. The possibility of replacing any or all of the components of the ZPs (i.e. zinc, phosphorus and oxygen) opens the door to numerous candidates for new AW additives. Although the simulations on which the theory is based were performed on simple model systems, we hope that the insight gained through the simulations will aid in selecting the most promising of these candidates in an efficient manner.

## Acknowledgements

The Natural Science and Engineering Research Council of Canada, General Motors of Canada Limited and General Motors Research and Development are gratefully acknowledged for financial support. Computational resources were made available by the Canadian Foundation for Innovation, the Ontario Innovation Trust, SHARCNet of Canada and the Academic Development Fund at the University of Western Ontario.

## References

[1] M. A. Nicholls, T. Do, P. R. Norton, M. Kasrai, and G. M. Bancroft. *Tribol. Int.*, 38:15, 2005.

[2] H. Spikes. *Tribol. Lett.*, 17:469, 2004.

[3] Z. Pawlak. *Tribochemistry of Lubricating Oils*. Elsevier, Amsterdam, 2003.

[4] J. M. Martin, C. Grossiord, T. Le Mogne, S. Bec, and A. Tonck. *Tribol. Int.*, 34:523, 2001.

[5] M. L. Suominen Fuller, M. Kasrai, G. M. Bancroft, K. Fyfe, and K. H. Tan. *Tribol. Int.*, 31:627, 1998.

[6] P. A. Willermet, D. P. Dailey, R. O. Carter III, P. J. Schmitz, and W. Zhu. *Tribol. Int.*, 28:177, 1995.

[7] E. S. Ferrari, K. J. Roberts, M. Sansone, and D. Adams. *Wear*, 236:259, 1999.

[8] M. A. Nicholls, P. R. Norton, G. M. Bancroft, M. Kasrai, G. De Stasio, and L. M. Wiese. *Tribol. Lett.*, 18:261, 2005.

[9] M. A. Nicholls, P. R. Norton, G. M. Bancroft, and M. Kasrai. *Wear*, 257:311, 2004.

[10] M. Fuller, M. Kasrai, J. S. Sheasby, G. M. Bancroft, K. Fyfe, and K. H. Tan. *Tribol. Lett.*, 1:367, 1995.

[11] J. S. Sheasby, T. A. Caughlin, and J. J. Habeeb. *Wear*, 150:247, 1991.

[12] M. Mee and A. A. Torrance. *Wear*, 128:201, 1988.

[13] N. J. Mosey, M. H. Müser, and T. K. Woo. *Science*, 307:1612, 2005.

[14] I. M. Hutchings. *Tribology: Friction and Wear of Engineering Materials*. Edward Arnold, London, 1992.

[15] J. M. Martin. *Tribol. Lett.*, 6:1, 1999.

[16] F. Rounds. *Tribol. Trans.*, 36:297, 1993.

[17] J. J. Habeeb and W. H. Stover. *ASLE Trans.*, 30:419, 1987.

[18] U. Landman, W. D. Luedtke, and J.P. Gao. *Langmuir*, 12:4514, 1996.

[19] N. J. Mosey, T. K. Woo, and M. H. Müser. *Phys. Rev. B*, In press.

[20] Z. Yin, M. Kasrai, M. Fuller, G. M. Bancroft, K. Fyfe, and K. H. Tan. *Wear*, 202:172, 1997.

[21] J. Haines, J. M. Léger, and G. Bocquillon. *Annu. Rev. Mater. Res.*, 31:1, 2001.

[22] M. Hebbache and M. Zemzemi. *Phys. Rev. B*, 70:224107, 2004.

[23] D. M. Teter. *MRS Bull.*, 23:22, 1998.

[24] M. Scherge, J. M. Martin, and K. Pöhlmann. *Wear*, In press.

[25] R. C. Coy and R. B. Jones. *ASLE Trans.*, 24:77, 1981.

[26] R. B. Jones and R. C. Coy. *ASLE Trans.*, 24:91, 1981.

[27] J. J. Dickert and C. N. Rowe. *J. Org. Chem.*, 32:647, 1967.

[28] J. S. Ashford, L. Bretherick, and P. Gould. *J. Appl. Chem.*, 15:170, 1965.

[29] H. Fujita and H. Spikes. *Proc. Ins. Mech. Eng. J*, 218:265, 2004.

[30] N. J. Mosey and T. K. Woo. Submitted.

[31] N. J. Mosey and T. K. Woo. *Tribol. Int.*, In press.

[32] N. J. Mosey and T. K. Woo. *J. Phys. Chem. A*, 108:6001, 2004.

[33] N. J. Mosey and T. K. Woo. *J. Phys. Chem. A*, 107:5058, 2003.

[34] H. Ji, M. A. Nicholls, P. R. Norton, M. Kasrai, T. W. Capehart, T. A. Perry, and Y.-T. Cheng. *Wear*, 258:789, 2005.

[35] M. Aktary, M. T. McDermott, and G. A. McAlpine. *Tribol. Lett.*, 12:155, 2002.

[36] G. M. Bancroft, M. Kasrai, M. Fuller, Z. Yin, K. Fyfe, and K. H. Tan. *Tribol. Lett.*, 3:47, 1997.

[37] J. S. Sheasby, T. A. Caughlin, A. G. Blahey, and K. F. Laycock. *Tribol. Int.*, 30:301, 1990.

[38] Z. Zhang, E. S. Yamaguchi, M. Kasrai, and G. M. Bancroft. *Tribol. Lett.*, 19:211, 2005.

[39] Y. Wan, L. Cao, and Q. Xue. *Tribol. Int.*, 30:767, 1997.

[40] Y. Wan and Q. Xue. *Tribol. Int.*, 28:553, 1995.

[41] M. A. Nicholls, P. R. Norton, G. M. Bancroft, M. Kasrai, T. Do, B. H. Frazer, and G. De Stasio. *Tribol. Lett.*, 17:205, 2004.

[42] G. W. Canning, M. L. Suominen Fuller, G. M. Bancroft, M. Kasrai, J. N. Cutler, G. De Stasio, and B. Gilbert. *Tribol. Lett.*, 6:159, 1999.

[43] J. F. Graham, C. McCague, and P. R. Norton. *Tribol. Lett.*, 6:149, 1999.

[44] O. L. Warren, J. F. Graham, P. R. Norton, J. E. Houston, and T. A. Michalske. *Tribol. Lett.*, 4:189, 1998.

[45] M. A. Nicholls, G. M. Bancroft, P. R. Norton, M. Kasrai, G. De Stasio, B. H. Frazer, and L. M. Wiese. *Tribol. Lett.*, 17:245, 2004.

[46] M. A. Nicholls, T. Do, P. R. Norton, G. M. Bancroft, M. Kasrai, T. A. Capehart, Y.-T. Cheng, and T. A. Perry. *Tribol. Lett.*, 15:241, 2003.

[47] J. Ye, K. Makoto, and Y. Yasuda. *Tribol. Lett.*, 13:41, 2002.

[48] B. S. Bec, A. Tonck, J. M. Georges, R. C. Coy, J. C. Bell, and G. W. Roper. *Proc. R. Soc. London A*, 455:4181, 1999.

[49] J. S. Sheasby, T. A. Caughlin, and W. A. Mackwood. *Wear*, 201:209, 1996.

[50] E. S. Yamaguchi, Z. Zhang, M. Kasrai, and G. M. Bancroft. *Tribol. Lett.*, 15:385, 2003.

[51] Z. Zhang, M. Kasrai, G. M. Bancroft, and E. S. Yamaguchi. *Tribol. Lett.*, 15:377, 2003.

[52] M. I. De Barros, J. Bouchet, I. Raoult, T. Le Mogne, J. M. Martin, M. Kasrai, and Y. Yamada. *Wear*, 254:863, 2003.

[53] M. Kasrai, M. Suominen Fuller, and G. M. Bancroft. *Tribol. Trans.*, 46:534, 2003.

[54] P. A. Willermet, D. P. Dailey, R. O. Carter III, P. J. Schmitz, W. Zhu, J. C. Bell, and D. Park. *Tribol. Int.*, 28:163, 1995.

[55] Najman M. N., M. Kasrai, G. M. Bancroft, B. H. Frazer, and G. De Stasio. *Tribol. Lett.*, 17:811, 2004.

[56] Najman M. N., M. Kasrai, and G. M. Bancroft. *Tribol. Lett.*, 17:217, 2004.

[57] Najman M. N., M. Kasrai, G. M. Bancroft, and A. Miller. *Tribol. Lett.*, 13:209, 2002.

[58] M. Scherge, D. Shakhvorostov, and K. Pöhlmann. *Wear*, 255:395, 2003.

[59] K. Masenelli-Varlot, M. Kasrai, G. M. Bancroft, G. De Stasio, B. Gilbert, E. S. Yamaguchi, and P. R. Ryason. *Tribol. Lett.*, 14:157, 2003.

[60] K. Varlot, J. M. Martin, C. Grossiord, B. Vacher, and K. Inoue. *Tribol. Lett.*, 6:181, 1999.

[61] K. G. Stanulov, H. N. Harhara, and G. S. Cholakov. *Tribol. Int.*, 31:257, 1998.