

The history and mechanisms of ZDDP

H. Spikes*

Tribology Section, Department of Mechanical Engineering, Imperial College, London SW7 2AZ, UK

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This paper reviews research into the mechanisms of action of the lubricating oil additive, zinc dialkyldithiophosphate (ZDDP). The development of the use and research into ZDDP is first charted historically, starting with the additive's first introduction in engine oils in the late 1930s. Then our current state of knowledge of each of the main facets of ZDDP behaviour both in solution and at metal surfaces is identified and discussed. It is concluded that we now know a great deal about the properties and morphology of ZDDP antiwear films but still relatively little about the reaction pathways that lead to ZDDP film formation or about the kinetics of ZDDP film generation and removal.

KEY WORDS: Zinc dialkyldithiophosphate, ZDDP, ZnDTP, antiwear, history, wear, lubricant additives

1. Introduction

Zinc dithiophosphates (ZDDPs) are arguably the most successful lubricant additives ever invented. They were introduced over 60 years ago, have been in continuous use ever since and are still being employed in practically all current engine oils. This longevity is all the more striking since strenuous efforts have been made by additive companies over the last 10 years to replace them, but in vain. It has so far proved impossible to identify any reasonably cost-effective compound having comparable antiwear performance to ZDDPs in engine oils.

As well as being remarkable in their performance, ZDDPs have also been astonishingly successful in their ability to inspire research. The last half century has seen an extraordinary number of published research papers describing investigations of how these additives behave in their triple role as antioxidants, corrosion inhibitors and antiwear agents.

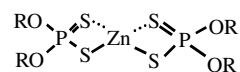
This paper reviews the history of ZDDPs as lubricating oil additives, from their genesis in the late 1930s to the present day. Based on this, the paper then assesses our current state of knowledge of the mechanisms by which these additives work. Finally some important outstanding research questions about the behaviour of ZDDP as an antiwear additive are highlighted.

Because of the enormous volume of ZDDP research literature, the scope of this review has been necessarily limited and it is confined mainly to research which has studied ZDDPs in simple solution, without the concomitant presence of other lubricant additives. It is recognised that ZDDPs are actually used in formu-

lated oils, blended with many other additives, some of which have been shown to interact with ZDDP. However, other additives appear to modulate rather than change the nature of ZDDP response and the mechanisms of ZDDP can be most clearly seen by studying it in simple solutions rather than blends. It should also be noted that this review focuses on research which has aimed to study the mechanisms by which ZDDP functions as a lubricant additive and has neglected the large body of more practical literature concerned primarily with wear and oxidation performance in bench tests and machine components.

A simple representation of the structural formula of ZDDP is shown below although, as discussed in section 4.1 of this paper, the molecular nature of ZDDP in solution is rather more complex than this figure suggests.

Two alternative, recent reviews of ZDDP are to be found in [1,2].



2. ZDDPs As lubricant additives

Figure 1 places the appearance of ZDDPs within the chronology of lubricant additive development in general. Oiliness additives were first discovered in 1918 and were immediately used to reduce friction in marine engine lubricants [3]. Most other additive classes, including pour point depressants, extreme pressure (EP) additives, viscosity modifiers, antioxidants, corrosion inhibitors and detergents, were introduced within one busy decade between 1930 and 1940, in response to

*E-mail: h.spikes@imperial.ac.uk

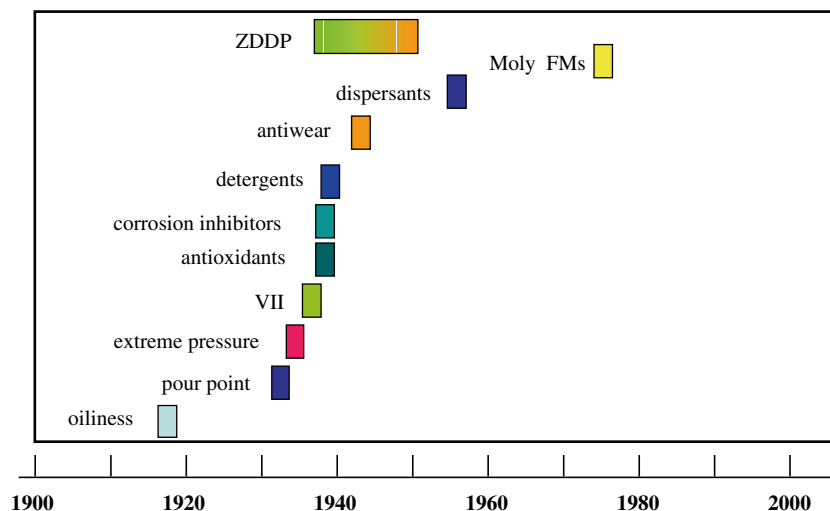


Figure 1. Chronology of development of main classes of lubricant additive.

practical performance problems arising in the rapidly developing motor car industry of the day. Antiwear additives were first developed primarily to meet problems in aviation applications [4,5] but, as will be shown in this paper, quickly became a crucial component of motor oils. By the mid-1940s, most additive classes had been identified, although within each class many new chemistries continued (and continue) to be developed.

The pace of additive development in the 1930s can be gauged from an address by Boehm to the API Annual Meeting Marketing Division in 1948 [6]; *“Ten years ago additives were looked upon by lubricating-oil manufacturers as costly gadgets, and it was not unusual to hear them disparagingly referred to as ‘mouse milk.’ However much has happened in the past 10 years. ...*

Thus we see a new business which, in the last 15 years has grown from practically nothing to a position of an important and substantial supplier to the lubricating-oil manufacturing industry”.

Towards the end of the 1930s there was rapidly growing interest in the use of phosphorus-containing compounds as lubricant additives, especially those containing both phosphorus and sulphur [7]. This is illustrated in figure 2 from a paper in 1952 by Smalheer and Mastin [8] which shows, on a year-by-year basis, the number of US patents granted in the field. (In their paper, these authors note that the decrease in patent numbers seen in the late 1940s was due not to less patents being filed but to inadequacies of the U.S. Patent Office).

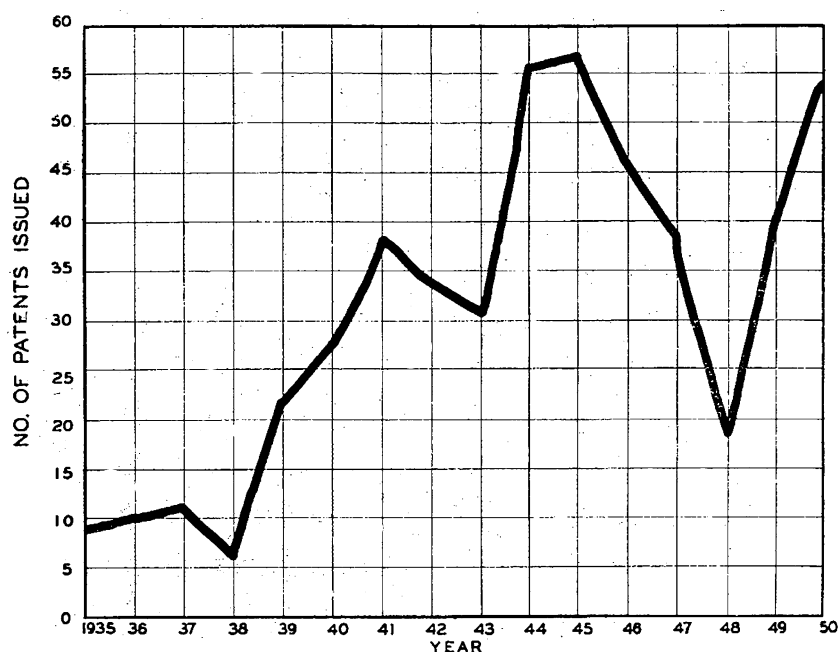


Figure 2. Number of lubricant P-S additive patents filed in the US on a year-by-year basis from 1935 to 1950 [8].

Within this general trend, ZDDPs first appeared formally on the lubricant additive stage in 1941 with the filing of four patents [9–11], one by the company Lubri-zol (the name remained hyphenated until 1943), one from American Cyanimid and two from the Union Oil Company. The Lubrizol patent concerned ZDDPs having cyclohexyl-based alkyl groups and the one from American Cyanimid metal dithiophosphates with capryl groups, while the Union Oil patents covered a much wider range of metals and alkyl structures. All three patents claimed ZDDPs as bearing corrosion and oxidation inhibitors in engine oils. Interestingly the Union Oil patents refer to a previous patent application in 1937 but this cannot be traced. Thus it seems probable that ZDDPs were first used in engine lubricants in the late 1930s.

The antiwear properties of ZDDP remained apparently un-noticed throughout the 1940s. In 1949 however, V8 engines having overhead valves and increased compression ratios were introduced, which resulted in greatly increased stresses on valve train components. This led to major cam and follower wear problems throughout the US and in 1955 it was found that oils which contained ZDDP generally gave less wear than those without it [12,13]. The result was a very rapid adoption of ZDDP within the automobile industry and, by 1958, as reported by Larson [14]; The compound type zinc dialkyl dithiophosphate has gained wide acceptance in the United States for high quality motor oils. Two out of three of the major United States automobile manufacturers either require zinc dithiophosphate at about 1% of an 80% concentrate in the initial fill in new automobiles or require qualification tests which only zinc dithiophosphate can pass. ... Current usage of zinc dithiophosphate in the United States is estimated at 30,000,000 pounds per year on a 100% active ingredient basis.

In the following 30 years there was relatively little change in the use of ZDDPs—they were employed in practically all engine lubricants and many transmission and industrial oils. During these years there was, however, a gradual optimisation of ZDDP structure to match different applications, engine types and formulation chemistries. This led, for example, by the 1980s, to more reactive, secondary alkyl ZDDPs being used in gasoline and more thermally stable, primary ones in diesel oils.

Table 1.
Phosphorus and sulphur limits in engine oil specifications.

1989	SG	No P, S limits
1994	SH, GF-1	≤ 0.12% wt. P
1997	SJ, GF-2	≤ 0.10% wt. P
2000	SL, GF-3	≤ 0.10% wt. P
2004	GF-4	0.06% wt. ≤ P ≤ 0.08% wt., ≤ 0.50% wt. S

In the 1990s, with the introduction of exhaust after-treatment catalysts it was realised that phosphorus oxides (and also sulphur oxides and ash) reduce the effective life of exhaust catalysts. This led to the progressive introduction of limits of the level of first phosphorus and recently sulphur in engine oils, as summarised in table 1. Since ZDDP is generally the only source of phosphorus in engine oils, this has put direct constraints on the concentration of this additive that can be employed and led, in turn, to great pressure to replace ZDDPs partially or wholly by other, phosphorus-free additives. One result of this seems to have been a huge increase in the level of research on ZDDP.

It is not yet clear whether the limits of phosphorus and sulphur in engine oils will be reduced further in future, leading perhaps to the eventual disappearance of ZDDP. Recently, attention has started to focus on the possibility of replacing a blanket limit on the level of phosphorus and sulphur in engine oils to a measure that better reflects the tendency of these elements to volatilise and thus reach the after-treatment catalyst [15]. This may eventually lead to a limit on P- and S-containing additive volatility or to a test which monitors these species in the exhaust and thus permits imaginative new formulations based on low volatility additives [13]. Whatever the future however, there is no doubt that the slow pace of reduction of phosphorus levels in engine oil specifications over the last 5 years reflects the remarkable effectiveness of ZDDP as an antiwear additive, and the great difficulty that additive companies have had in finding a replacement with comparable performance.

3. History of research on ZDDPs

Research aimed at discovering the mechanisms of action of ZDDPs began in earnest in the 1950s with

Table 2.
Introduction of experimental tools to study ZDDPs.

1950s	Wet chemistry Radiotracer techniques, ³² P, ³⁵ S, ⁶⁵ Zn Optical interference microscopy
1960s	GC, GC/MS Infrared spectroscopy XRF
1970s	XPS Auger SIMS ¹ H and ³¹ P NMR
1980s	STEM EELS EXAFS
1990s	Cryogenic surface analysis XANES AFM and other nanoprobes
2000s	X-PEEM Spacer layer interferometry

the recognition of their antiwear properties. This research has continued unabated ever since and its progression has very much been controlled by the availability of analytical and related experimental tools. This is exemplified in table 2.

In the sections below, the evolution of research on ZDDPs is charted from the 1950s through to the present day. Where possible, reference is made to technical journal papers rather than conference proceedings since the former are probably more accessible to the average reader.

3.1. Research in the 1950s

In the 1950s, analytical tools were limited primarily to wet chemistry and radiotracer methods, so research on ZDDPs was based on these techniques in combination with friction and wear measurements and astute observation. Despite these limitations, remarkable progress was made. Using ^{32}P radiotracing it was shown that ZDDPs form thick films on rubbed surfaces, containing up to $10\ \mu\text{g}/\text{cm}^2$ of P [16], which corresponds to a thickness of approximately 120 nm, assuming a density for zinc metaphosphate glass of $2.8\ \text{g}/\text{cm}^2$, i.e., a zinc density of $0.82\ \text{g}/\text{cm}^3$ [17]. This film was formed only within the rubbing track in a tappet tester operating at quite low temperatures, but a similar thickness was produced on un-rubbed specimens during extended immersion at $150\ ^\circ\text{C}$. The film was not significantly removed by treatment with solvents including toluene and water but was almost wholly removed by dilute HCl [18]. Combined ^{32}P and ^{35}S radiotracing showed that, while the ratio of P:S was 1:2 in the additive, it was much higher, reaching 8:1, in the antiwear film [19]. Research was also carried out in which a film was formed in rubbed contact and the ZDDP solution was then replaced by a ZDDP-free one [16]. This showed that the antiwear film was in effective dynamic equilibrium between chemical formation and mechanical removal.

In addition to radiotracer studies, revealing work was also carried out using optical interference microscopy to study the morphology of the reaction films formed on rubbed surfaces [20]. This showed that ZDDP reaction films were relatively rough at a microscopic scale, an observation that has recently become important in interpreting their friction properties. In the Discussion following Ref. [20] there is also one of the first published descriptions of the dependence of ZDDP antiwear activity (and thermal instability) on alkyl group structure, with the ranking of antiwear effectiveness [21].

secondary alkyl > primary alkyl > aryl

Considering the very limited tools available, astonishing progress to elucidate the nature of ZDDP films was made in the 1950s. This is illustrated by Larson in 1958 who describes a ZDDP corrosion inhibiting film on a bearing surface as; “*The end result of decomposition which involves stripping three or more of the alkyl groups and $1\frac{1}{2}$ sulphur atoms from the molecule leaves a largely inorganic residue. This residue is possibly a cross-linked polymer similar to a metaphosphate [14]*”.

3.2. Research in the 1960s

While research in the 1950s focussed on the nature of ZDDP antiwear films and their effectiveness, most of that in the 1960s was directed at understanding ZDDP solution chemistry. This reflects the availability of chromatographic tools such as GPC and GLC to analyse volatile reaction products and also the arrival of IR as a widely used analytical instrument. Many studies of the thermal decomposition of ZDDP were made in the 1960s [22–31]. All noted broadly the same pattern of chemical behaviour and each suggested a slightly different reaction mechanism. The proposed mechanisms will not be described in detail here since

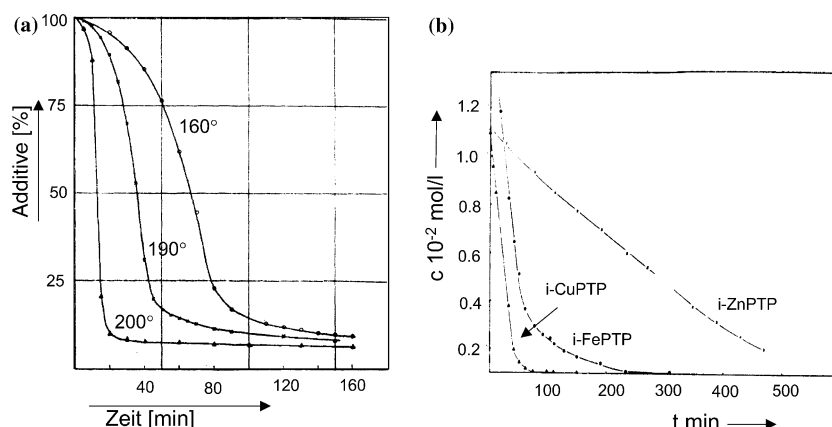


Figure 3. Thermal degradation of metal dithiophosphates. (a) Influence of temperature on thermal degradation rate of zinc dithiophosphate [25], (b) Thermal degradation rates of three metal dithiophosphates [31].

they have, to a large extent, been superseded by more recent work but the main experimental findings are worth summarising, as follows.

- (i) ZDDPs in hydrocarbon solution undergo an autocatalytic, thermally activated decomposition reaction which becomes significant above about 150 °C and rapid above about 180 °C. This is illustrated in figure 3(a) taken from Luther *et al.* [25]
- (ii) The main volatile products generated are mercaptides, alkyl sulphides, H₂S and olefins. The mercaptides and sulphides are formed directly and not from subsequent reaction between H₂S and olefins. No olefins of higher molecular weight than the original alkyl chain on the ZDDP are produced.
- (iii) The other main product is glassy and insoluble and contains phosphorus, oxygen, zinc with possibly some sulphur.
- (iv) ZDDP thermal decomposition is acid-catalysed but not accelerated by the presence of oxygen.

In terms of reaction mechanisms to be discussed later in this paper, two interesting implications noted at the time are; (a) that the formation of mercaptides and alkylsulphides suggests transfer of alkyl groups from oxygen to sulphur [28–30] and; (b) the lack of formation of higher alkanes, together with acid catalysis, supports a nucleophilic/electrophilic process more strongly than a free radical one [26].

As well as the above thermal decomposition work, surface film analysis was carried out in the 1960s using the newly available tools of reflection absorption infrared spectroscopy (RAIRS) and X-ray fluorescence (XRF). Francis and Ellison showed how RAIRS could be used to analyse ZDDP reaction films on heated metal surfaces [32] while Rounds employed XRF to obtain an elemental analysis of the reaction films formed by ZDDPs on rubbed surfaces [33]. Rounds found that the films formed were “several hundred monolayers thick” and, in confirmation of previous work, contained a larger P:S ratio than the original additive. He concluded that temperature was the key driving form in forming ZDDP tribofilms, with films being forming at rapidly in rubbing contact due to frictional flash temperature rise [34].

Another research theme in the 1960s was investigation of the effect on performance of replacing zinc in dithiophosphates by other metals [27,29,31,35,36]. This is complicated by the fact that there are a various responses of interest (e.g., antiwear and EP performance, induction time, rate of thermal decomposition) and metal dithiophosphates (MDDPs) rank differently against these. Figure 3(b) compares the rate of thermal degradation of three MDDPs [31]. More recent work on the influence of metal type and also alkyl structure on

ZDDP performance can be found in [37] where it was concluded that of all the MDDPs, those of zinc combine good antiwear effectiveness and thermal stability with relative non-toxicity. One interesting observation was that the metal ion in MDDP is labile and thus can be exchanged by other metal ions present and, if exchange occurs with a metal to produce a less thermally stable MDDP, rapid decomposition can result [31]. This will be further discussed in sections 4.2, 4.4 and 4.5 below.

The 1960s and early 1970s also saw much research on the oxidation inhibition mechanism of ZDDP and it was shown that ZDDP acts as both a peroxide decomposer and to destroy peroxy radicals [38–40].

3.3. Research in the 1970s

There was a relative lull in ZDDP research in the 1970s, but even so, two important new strands of research can be identified. One of these was the first application of the newly available vacuum-based, surface analysis techniques of XPS (ESCA), Auger, SIMS and EDAX to study the chemical composition of ZDDP antiwear films [41–43]. This showed that these films on steel were patchy and, in confirmation of earlier radiotracer work, contained a much higher P:S ratio than ZDDP itself [41,42]. XPS [41] and Auger electron spectroscopy (AES) [43] with successive ion etching was used to obtain profiles of the film composition for the first time, which suggested a complex film structure, with a lowermost layer of S-rich material, covered with patches of a P/Zn rich film containing less S. The overall thickness of the film was estimated to be about 1000 monolayers [43] or 50–100 nm [44]. Comparison was also made between films formed during rubbing (tribofilms) and those generated thermally by immersion in heated solution (thermal films) and it was concluded that chemistry of the two were similar [41]. Electrical contact resistance

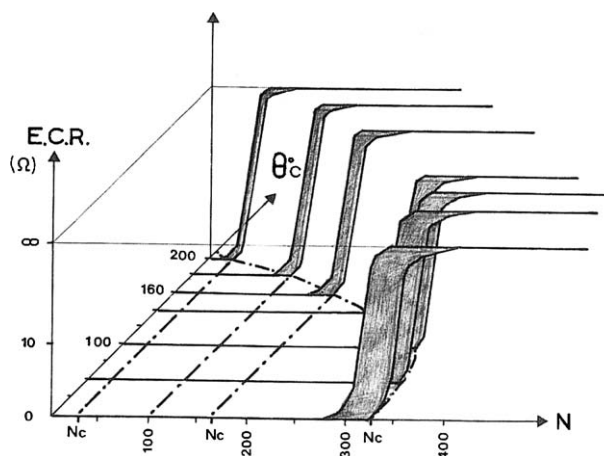


Figure 4. Influence of temperature on delay in ZDDP film formation measured by ECR. Reprinted from Wear Vol. 53, Georges J.M., Martin J.M., Mathia, T., Kapsa Ph., Meille G., Montes H., Mechanism of boundary lubrication with zinc dithiophosphate, pp. 9–34 copyright 1979, with permission from Elsevier.

(ECR) measurements were also employed to show the formation of an insulating reaction film after a temperature-dependent induction period [43–46], as illustrated in figure 4 [43]. The ECR method has continued to be a valuable way to study the kinetics of ZDDP film build up to the present day [47].

The second main strand of research, in the late 1970s, was application of ^1H - and ^{31}P -NMR to study the solution degradation products of ZDDP. Using these techniques, Coy and Jones [48] identified a wide range of species formed during ZDDP thermal decomposition including several thionyl species, where the alkyl groups of ZDDP had become linked to P by sulphur atoms. Based on this and on reference to the chemical literature, the authors proposed an O/S exchange mechanism for ZDDP reaction and film formation [49]. This will be further discussed in Section 4.4 below. The NMR approach continued to be applied by Spedding and Watkins [50] in the early 1980s who confirmed the O/S exchange phenomenon although they suggested a quite different reaction mechanism for ZDDP reaction, based on hydrolysis.

3.4. Research in the 1980s

From the very considerable research on ZDDPs in the 1980s, four main themes can be discerned. The first was simply an extension of work in the preceding decade using the vacuum-based techniques of XPS, Auger and SIMS to obtain progressively more accurate analysis of the films formed by ZDDP, on both on heated and rubbed surfaces [51–57]. As instruments became more sensitive, more detailed and informative analysis was possible, a trend which has continued through to the present. Palacios used EDAX to carry out very careful determination of the thickness of the ZDDP tribofilm and how this varied with load, rubbing time

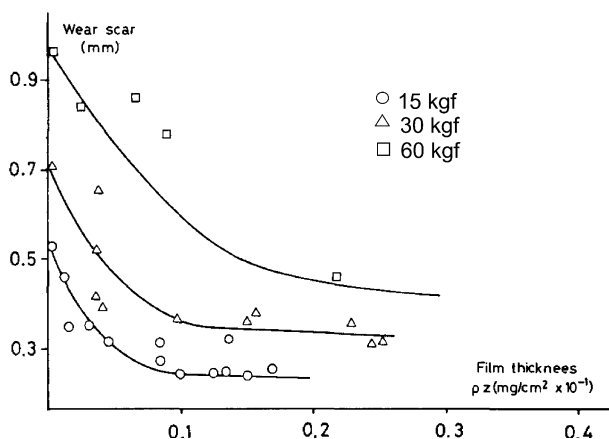
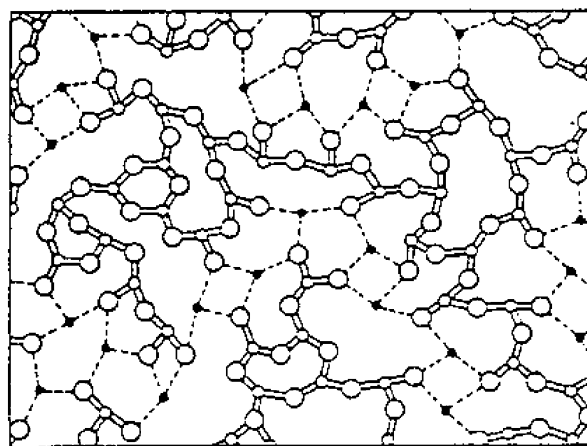


Figure 5. Correlation between ZDDP film thickness and the wear scar, 600 rev min⁻¹, 50 °C, 1 h. Reprinted from *Wear* Vol. 114, Palacios, J.M., Films formed by antiwear additives and their incidence in wear and scuffing, pp. 41–49, copyright 1987, with permission from Elsevier.

and ZDDP concentration [54,55]. He showed that ZDDPs formed films up to $\approx 40 \mu\text{g}/\text{cm}^2$ ($\approx 140 \text{ nm}$) thick although full antiwear protection was actually provided by a reaction film thicknesses of only $15 \mu\text{g}/\text{cm}^2$ (i.e. $\approx 50 \text{ nm}$) (figure 5).

A new strand of work was study of the adsorption behaviour of ZDDP on metal surfaces [58–60]. Dacre and Bovington [59] applied ^{13}C and ^{65}Zn radiotracing to show that adsorption of ZDDP was stronger on iron than on bearing steel. On the latter, ZDDP adsorbed physically and reversibly below 40 °C to form a monolayer, with this film becoming chemically adsorbed as the temperature was raised. At temperatures of 60 °C and above, on both iron and steel, a rapid loss of Zn took place from the adsorbed film.

A third new theme of the 1980s was initiated by Martin *et al.* who applied a variety of vacuum-based, analytical techniques including XPS, AES, scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), X-ray adsorption fine structure analysis (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) to determine the composition and structure of wear particles formed during rubbing with ZDDP-containing lubricants [61–64]. This showed that the particles were wholly amorphous and were essentially composed of a zinc(II)/iron(III) phosphate glass (figure 6) with the Fe(III) in octahedral sites. The authors suggested that the presence of Fe(III) indicated that iron oxides had



- oxygen atoms
 - phosphorus atoms
 - “modifier” cations (Zn, Fe)
- solid lines: covalent bonds
dotted lines: ionic bonds

Figure 6. Schematic diagram of structure of a metallic glass. Reprinted from *Trib. Trans.* Vol. 32, Belin, M., Martin, J.M., Mansot, J.L., “Role of iron in the amorphization process in friction-induced phosphate glasses”, pp. 410–413, copyright 1989, with permission from STLE.

been chemically “digested” by the phosphate and proposed that this process might be an important mechanism for alleviating wear by removing hard and abrasive Fe_2O_3 particles.

The fourth main focus of research during the 1980s was study of the influence of oxygen and oxidants on ZDDP film formation and activity. Willermet [65,66] showed that, when ZDDP acted in its role of a peroxy-radical/peroxide decomposer, the products no longer prevented wear [65,66]. (This finding has recently been confirmed in a detailed study using ^{31}P -NMR [67]). However in apparent contradiction of this, Willermet also showed that oxygen gas itself assisted in the anti-wear action of ZDDP, which gave higher wear in nitrogen atmosphere than in air [68]. It was found that a number of different compounds as well as oxygen were able to promote ZDDP activation and Willermet suggested that this phenomenon might result from an initial electron transfer. In related work, Habeeb and Stover showed that peroxides present in lubricant act to promote wear and they suggested that one of the mechanisms by which ZDDP reduces wear was by the additive decomposing peroxides and thus preventing the latter's pro-wear action [69]. A similar conclusion was later reached by Rounds [70].

3.5. Research in the 1990s

Towards the end of the 1980s, it was recognised that the rigorous cleaning needed before lubricated-coated

specimens could be subjected to vacuum-based, surface analytical methods might disturb or even remove important components of antiwear films and thus provide a misleading picture of the nature of these films [71]. In the 1990s, attention thus focussed on “in-lubro” ways of studying rubbed surfaces. In practice there have turned out to be a hierarchy of such methods; “in-contact” (i.e., study within the rubbing contact itself), “in situ” (within the rubbing test apparatus without removing supernatant oil) or “in-lubro” (removed from the tribometer but still uncleaned and covered with the original test lubricant).

One technique was to rapidly freeze components taken straight from rubbing tests in liquid nitrogen and then handle and analyse these by vacuum-based techniques using cryogenic and cold-stage methods developed for studying biological samples [72,73]. Using this approach, dynamic SIMS depth profiling showed the presence of hydrocarbon material 100 nm deep within the ZDDP reaction film, leading the authors to propose the presence of a supernatant hydrocarbon-rich layer on top of the ZDDP film. This simple picture was confused, however, when deuterated ZDDP was studied, since in this case a higher concentration of deuterated species relative to protonated was found in the outer layer of the film than deeper within it [74].

A second in-contact technique, developed and applied by Sheasby in the early 1990s, was direct visual observation through the transparent surface of a lubricated contact formed between a steel ball and

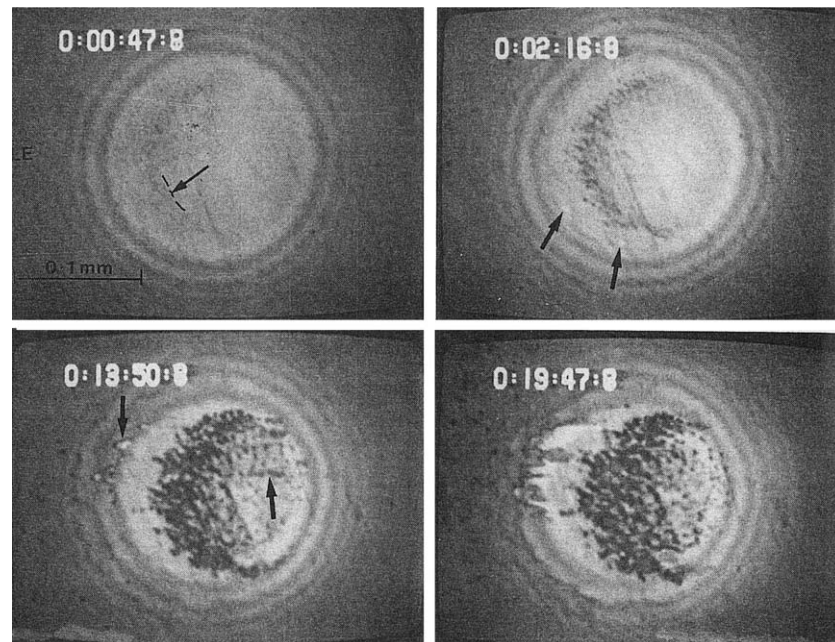


Figure 7. Optical images of a sapphire flat sliding on a steel ball lubricated with ZDDP showing development of pad-like structure in the inlet. Reprinted from *Wear* Vol. 150, Sheasby, J.S., Caughlin, T.A., Habeeb, J.J., Observation of the antiwear activity of zinc dialkyldithiophosphates additives, pp. 247–257, copyright 1991, with permission from Elsevier.

sapphire or glass disc [75]. This showed that the ZDDP formed a “friction-polymer”-like material in the contact inlet, which in turn led to the development a dynamically varying, pad-like structure within the contact itself. Figure 7 is a series of images from a 20 min rubbing test showing the formation of a thick “polymeric” layer in the contact inlet on the left and the eventual development of a pad-structure in the contact centre [75].

As well as visual observation, by choosing suitable transparent surfaces, in-contact IR spectroscopy of the lubricating film in and around the contact can be carried out [76] and this has recently been used to show the in-contact generation of inorganic phosphates by ZDDP [77]. *Ex situ* infrared work has also been carried out on ZDDP reaction films which suggests that these are primarily amorphous ortho- and pyrophosphates rather than polyphosphate glasses [78].

Perhaps the most versatile in-lubro approach, which began the 1990s but continues to be heavily applied, is the application of atomic force microscopy (AFM) and related nano-probe and nano-indentation techniques to study lubricant films. These methods do not require the test surface to be rigorously cleaned and can, indeed, be applied to surfaces covered with supernatant oil. AFM and lateral force microscopy have been used to determine both the morphological and the physical properties of ZDDP tribofilms [79–84]. This has confirmed that these films are microscopically rough, with a structure consisting very smooth and flat, plateau-like pads separated by deep valleys. In recent work the evolution of these pads with rubbing time at 100 °C has been examined using AFM and it has been shown that they initially develop as widely spaced, small islands of film which gradually extend until an almost complete film is developed [84]. As well as the morphology, the physical properties of hardness and stiffness of ZDDP films, which are likely to determine the film’s mechanical survival as well as the stresses experienced by the substrate, have been estimated by nano-indentation techniques [79–85].

In an important study in 1999, Bec *et al.* [85] converted a surface forces apparatus into a sliding nanoindenter and used this to study the morphology and physical properties of surfaces rubbed in ZDDP solution but still covered with supernatant test fluid. This resulted in two novel observations. One was that the solid-like ZDDP reaction film was covered with a micron-thickness, viscous liquid layer which, by reference to earlier cryogenic studies [73,74], the authors ascribed to oligomeric, phosphate-rich material. The second main finding of this work was that the antiwear film appeared to increase in hardness and elastic modulus during nanoindentation. However when material was removed from the surface by abrasion, the hardness was found to be unchanged from its original value. In the parlance of the day the authors termed this the

response of a “smart” material. The above findings are discussed in more detail in sections 4.7 and 5.3 below.

As well as the above *in situ* work, chemical analysis of the tribofilms formed by ZDDP using surface analytical techniques continued to progress in the 1990s and X-ray absorption near-edge spectroscopy (XANES) became a particularly important tool. The two main advantages of XANES are that (i) it can provide quite clear discrimination between atoms of the same elements having only very slight differences in their electronic and thus chemical environment and (ii) it has different modes of operation that enable both very thin surface layers to be analysed separately on the same specimen. Disadvantage of XANES, along with other X-ray spectroscopies, are that it is not possible to predict or interpret the spectra produces *a priori*, so spectra have to be interpreted by comparison with reference chemicals and it is not quantitative. Since its first application in 1989 [64], many papers based on the application of XANES to study ZDDP films have been published e.g., [86–95] and several new findings of importance have emerged. Most of these will be described in sections 4.6 and 4.7 below, but perhaps the key information that XANES work has provided is that the pads in the antiwear film consist of a thin surface film, rich in quite long chain polyphosphate on top of shorter chain poly- or orthophosphate glass material [88–90] and strong confirmation that the tribofilms, formed on rubbed surfaces have similar composition to thermal films [89–91]. (The main forms of phosphate glass are described in Appendix A).

3.6. Research in the 2000s

Surface analytical techniques have continued to be applied extensively to study ZDDP films during the current decade. The use of existing techniques has been refined. Martin *et al.* [95] has combined XANES with AES, SIMS and XPS to show that, while the main cation present in the upper levels of the tribofilms pads is zinc, the proportion of iron to zinc increases progressively towards the metal surface. This study also showed that sulphur was present in the pads in the form of zinc sulphide. The potential of focussed ion beam (FIB) to delicately section a worn surface for subsequent analysis of the tribofilm has also recently been demonstrated [96]. Eglin *et al.* have developed an ingenious method for producing a series of tribofilms generated under different conditions from one test, for subsequent surface analysis, the so-called “combinatorial approach” [97]. One new analytical method which has become available is X-ray photoemission microscopy (X-PEEM), in which secondary electron micro-images are obtained in parallel with XANES to effectively produce XANES-type images of the surface composition. This has demonstrated that the surfaces of larger pads in the ZDDP antiwear film contain very

long chain polyphosphate while those of smaller pads consist primarily of short chains [98,99].

In addition to surface analysis and AFM, a significant new approach has been the development of an *in situ* optical interference method of monitoring ZDDP tribofilm thickness using space-layer interferometry (SLIM). In the 1990s interferometry was employed to study the formation of ZDDP films in a rolling steel ball on glass flat contact at a range of temperatures and showed that ZDDPs form solid-like films up to 20 nm thick at temperatures above 150 °C [100]. This work could only be carried out using rolling contact conditions since the optical coatings required for interferometry were rapidly abraded in the thin film, sliding conditions necessary to generate ZDDP tribofilms. The ZDDP films studied were thus essentially thermal films. In 2001, this limitation was overcome by using *in situ* but out-of-contact SLIM. In this, a steel ball is rubbed against a steel disc in a ZDDP-containing lubricant to generate tribofilms. Periodically throughout a test, rubbing motion is halted and a spacer-layer coated glass disc is pressed against the wear track on the ball and an interference image of any separating film present is obtained. This enables the thickness of the ZDDP tribofilm to be measured and monitored as a function of rubbing time without disturbing the film: (the surfaces remain at the test temperature and are not cleaned in any way prior to measurement) [101–105].

Figure 8(a) illustrates the gradual build up of a solid-like reaction film in a ZDDP-lubricated, rubbed track at 100 °C as indicated by optical interference

while figure 8(b) shows the corresponding mean film thickness build up with rubbing time [104].

4. Current understanding of ZDDP

The aim of the preceding section was to show how research on ZDDP has developed over the last 60 years and thus place in context our current knowledge of ZDDP behaviour, while also highlighting some past research that may not have received as much recent attention as appropriate. In this section, our existing state of knowledge is assessed. Figure 9 shows the various stages in ZDDP action, all of which have been subjected to considerable research scrutiny and each of which will be discussed separately below.

4.1. Molecular Nature of ZDDP in solution

Both NMR [106] and vibrational spectroscopy [107] have shown that ZDDP exists as an equilibrium between monomer and dimer in solution, as illustrated in figure 10. This equilibrium moves to favour the monomer as temperature is increased and, in both structures, four sulphur atoms are arranged equivalently in a tetrahedron around the zinc. The above studies were, however, carried out in quite polar solvents, and more recent, dynamic light scattering (DLS) work has suggested that there may also be tetrameric and even higher ZDDP structures present in low polarity mineral oil solution [108]. This is supported

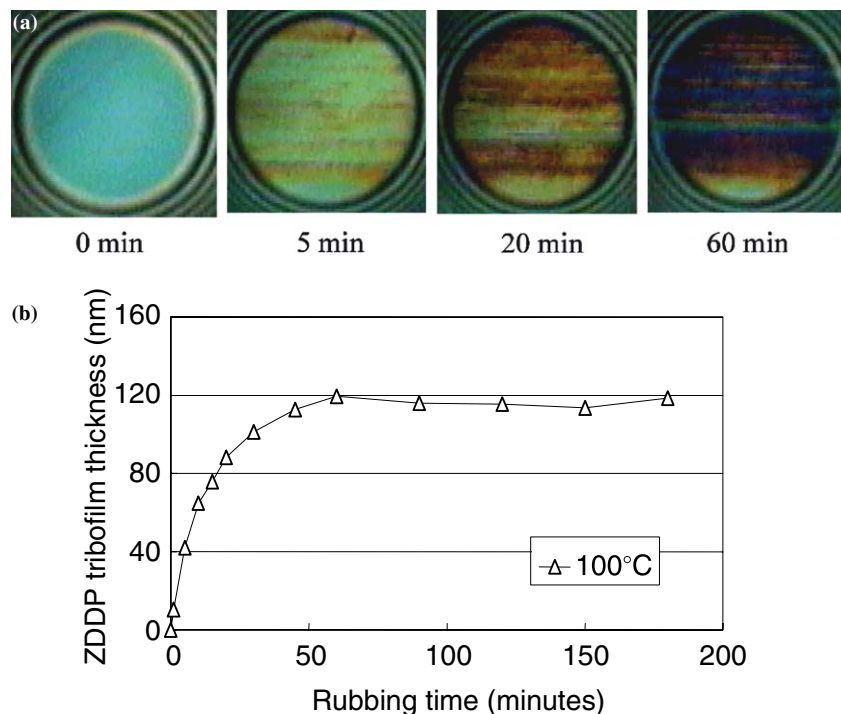


Figure 8. Use of *ex situ* interferometry to monitor ZDDP tribofilm. (a) sequence of interference images showing tribofilm formation by ZDDP on steel ball, (b) Mean film thickness of ZDDP tribofilm over time.

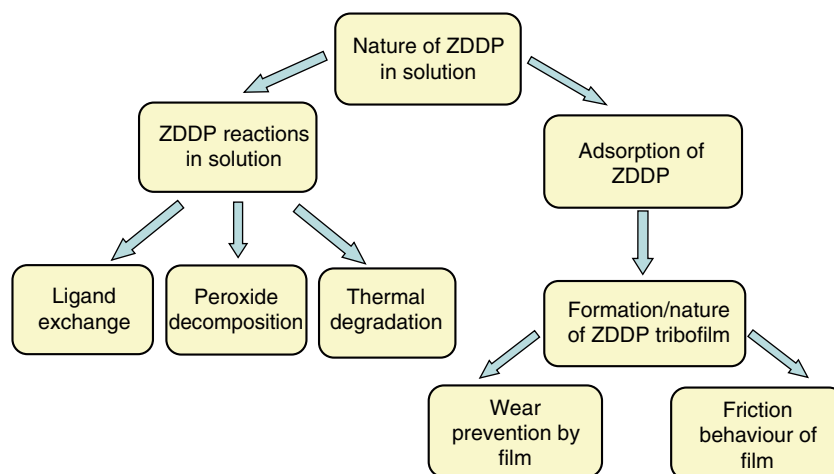


Figure 9. Main stages of ZDDP behaviour.

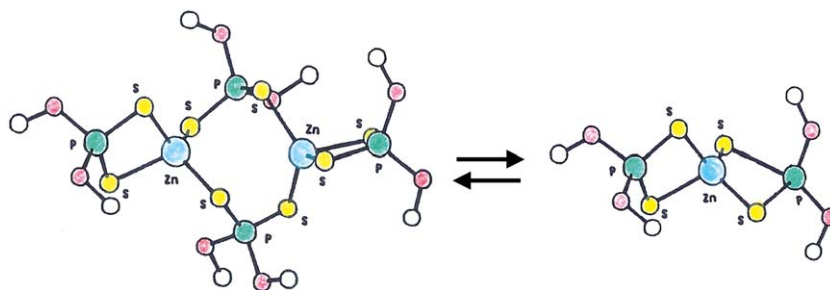
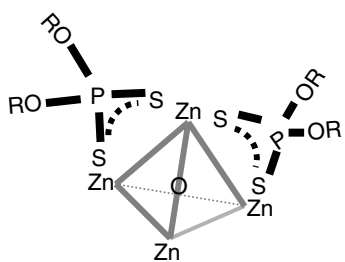


Figure 10. Equilibrium between dimeric and monomeric ZDDP forms.



basic-ZnDTP, (DTP)₆Zn₄O
(two of four DDP ligands shown)

Figure 11. Structure of basic ZDDP.

by the fact that some ZDDPs form polymeric structures in the solid state [109].

The structures illustrated in figure 10 are of neutral ZDDP. It has been known for many years that ZDDP can also exist in a basic form [110], with the molecular structure in solution shown in figure 11 [67]. Basic ZDDP can convert to the neutral form and ZnO at elevated temperature [111]. A number of studies have compared the antiwear [112], film-forming [90] and antioxidant [113] properties of the neutral and basic forms. While some of these have shown slight differences, especially in terms of low temperature adsorption properties [32,114,115] and engine

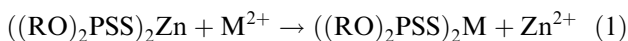
wear [116], in general the two forms appear to behave quite similarly.

As well as the above experimental work, semi-empirical quantum mechanical calculations have been carried out to determine the theoretical configurations and relative stabilities of the various ZDDP forms [117]. This has predicted similar structures to those identified experimentally and suggested that the basic and dimeric forms are more stable than monomeric ZDDP, with long alkyl chains favouring the stability of the dimer over the monomer. From all the above, it is likely that, while the basic and neutral ZDDPs may show slightly different levels of reactivity, the mechanisms by which they act as antioxidants or as antiwear additives are probably essentially the same.

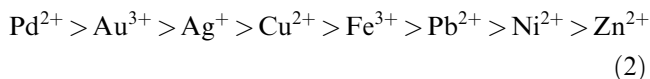
As indicated in figure 9, the literature suggests that ZDDPs can show three different types of chemical behaviour in solution, ligand exchange, antioxidant activity, and thermal degradation.

4.2. Ligand exchange by ZDDP

One feature of ZDDPs that may play a role in their antiwear activity is that the dithiophosphate ligands are labile, so the zinc cation can be quite easily exchanged by another metal ion such as Fe or Cu to form a less thermally stable MDDP [31], e.g.,



This may take place in solution and also, as will be discussed in section 4.5 below, at metal oxide surfaces. Dithiophosphates are metal extraction agents [118] and the ability of one metal cation to displace another in MDDP has been thoroughly investigated. The relative order of extraction is



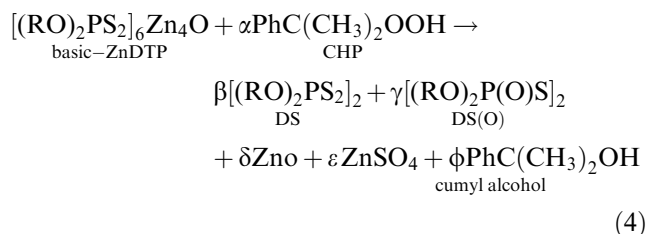
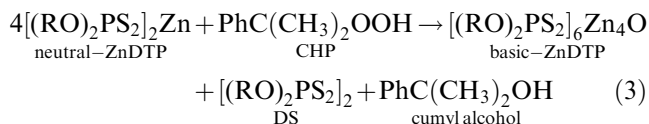
so that cations to the left will displace cations to the right from MDDP [119]. Recently, the ligand exchange properties of ZDDP have received further attention because it has been shown that when ZDDP is blended with the friction modifier additive, molybdenum dithiocarbamate, an equilibrium mixture of Mo and Zn dithiocarbamates and dithiophosphates is formed in oil solution which may influence the friction modifier response [120,121].

4.3. Oxidation inhibition by ZDDP

ZDDPs were recognised to be highly effective oxidation inhibitors in engine oils in the early 1940s [9–11], and in the 1950s it was shown that this arose from their ability to decompose hydroperoxides [122]. Then, in the 1960s, it was found that ZDDPs also decompose peroxy-radicals [38–40]. This combined action makes them very effective in quenching the peroxide oxidation cycle which is at the heart of the hydrocarbon

oxidation chain reaction. When ZDDPs react with hydroperoxides and peroxy radicals they generate products which themselves act as effective oxidation inhibitors [123], making ZDDP a highly efficient inhibitor. Although the overall reaction process by which ZDDPs act as peroxide and peroxy-decomposers is well accepted, there is less consensus concerning the main chemical equations involved and Willermet has summarised the various suggested antioxidant reactions of ZDDP, as shown in figure 12 [124].

There is agreement that when ZDDPs act in their peroxide-decomposing role, the species that they form are no longer able to produce effective zinc phosphate antiwear films [65,66]. In a recent, systematic study of the impact of cumene hydroperoxide (CMP) on ZDDP it was shown that above a critical peroxide:ZDDP ratio, antiwear activity is largely lost and the main reaction products are dithiophosphate mono- and di-sulphides and either ZnSO₄ or ZnO, as shown in equations 3 and 4 from [67].



ZDTP: zinc dialkyldithiophosphate; $[(RO)_2P(S)S]_2Zn$
 HDTP: dithiolic acid; $(RO)_2P(S)SH$
 BZDTP: basic ZDTP; $[(RO)_2P(S)S]_6Zn_4O$
 DS: $(RO)_2P(S)S-SP(S)(RO)_2$; DS*: $(RO)_2P(S)S\cdot$

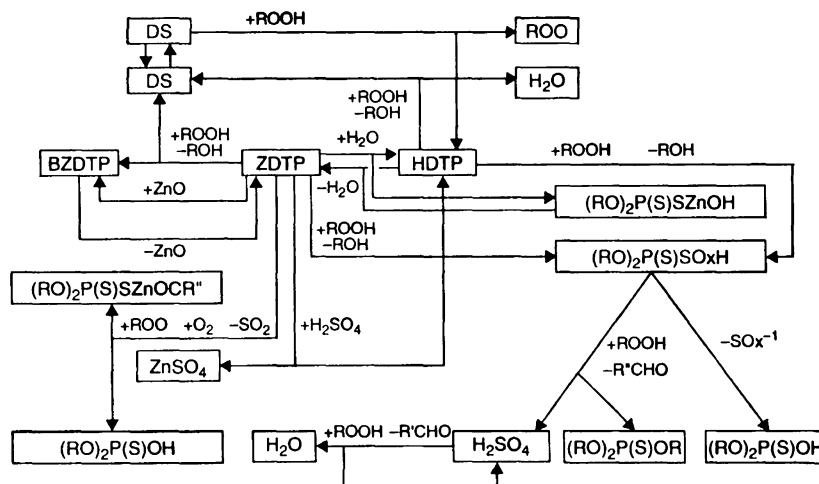


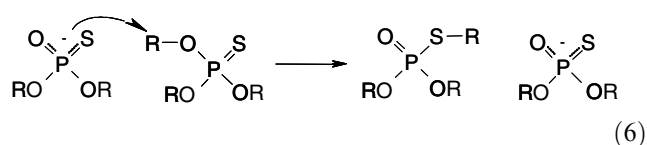
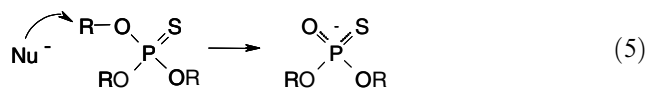
Figure 12. Schematic diagram of main antioxidant mechanisms of ZDDP. Reprinted from Lubr. Sci. Vol. 9, Willermet, R.A., Carter, R.O., Schmitz, P.J, Everson, M. Scholl, D.J. and Weber, W.H., "Formation, structure and properties of lubricant-derived antiwear films", pp. 325–348, copyright 1997, with permission from Leaf Coppin.

Although attention has focussed on the peroxide and peroxy-radical decomposing properties of ZDDPs, it should be recognised that they are also very effective metal deactivators, able not only to sequester copper, lead and iron in solution but also to produce thermal reaction films on metal surfaces, as will be discussed in section 4.6 below, and thus prevent these metals releasing pro-oxidant ions to the liquid phase. A key factor here is that pro-oxidant metal cations are generally multivalent ones, such as those of iron, lead and copper, which catalyse redox reactions while monovalent zinc cations are relatively harmless. There is thus a benefit in replacing the former by the latter in oil solution.

4.4. Thermal degradation of ZDDP

In the absence of significant levels of hydroperoxides or peroxy-radicals, ZDDPs (and their ligand exchange products) react in solution at high temperatures by a very different, thermal or thermo-oxidative degradation route, which leads to a zinc phosphate solid deposit, alkyl sulphides, mercaptans, hydrogen sulphide and olefins [25–31]. The temperature of this degradation process is dependent on the alkyl groups present (and the metal cation) but usually occurs somewhere between 130 and 230 °C.

In the 1960s, there was considerable debate about the mechanism of thermal degradation but this was resolved in an important paper by Jones and Coy in 1981 [49]. In early work there had been recurring evidence of exchange between O and S in ZDDP molecules, with the alkyl groups, which are initially bonded to oxygen atoms in ZDDP, being transferred to the sulphur atoms [28–30]. This was confirmed by Coy and Jones using ^1H - and ^{31}P -NMR [48], who noted that this O/S exchange represents a well-known property of organic thiophosphates. These compounds were, (and still are), an important class of insecticides, which has led to a large body of research into their chemical behaviour, as described by Hilgetag and Teichmann [125,126]. A key chemical feature of organothiophosphates is that they are very strong alkylating agents, with an initial reaction with a nucleophile Nu^- of the form shown in equation 5 below, followed often by autocatalytic realkylation [125]

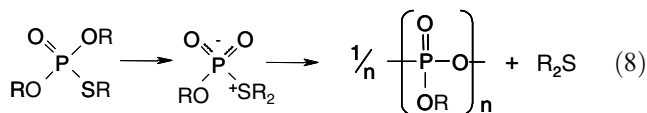


Mercaptides are suitable nucleophiles for this reaction but thiophosphates themselves are sufficiently nucleophilic that they can self-alkylate when heated in the absence of other nucleophiles.

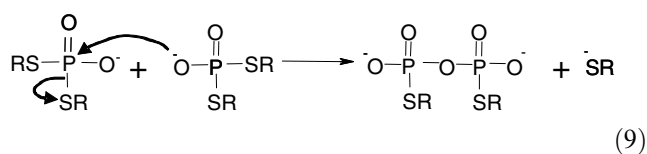
Dithiophosphates $(\text{RO})_2\text{PSS}^-$ are even stronger alkylating agents than thiophosphates and self-alkylation can occur twice to give the O/S exchange isomer, dithionylphosphate $(\text{RS})_2\text{POO}^-$ [125]. Thus ZDDPs isomerise to form the dithionyl species at relatively modest temperatures and even at room temperature in the presence of some Lewis acids [126].



This alkylation reaction has two important consequences. One is that it leads to very easy transalkylation, in which alkyl groups are exchanged between different molecules in heated ZDDP solution. The second is that the RS groups formed in the thionyl or dithionyl phosphates are subsequently very easily displaced by attack of a phosphoryl group from a neighbouring molecule to form a polyphosphate. Thus for the thionylphosphate [125];



According to the above, the dithiophosphate should polymerise to form the polythiophosphate.



The question then arises as to how the remaining sulphur is lost to form the almost sulphur-free polyphosphate glass that is often observed? Jones and Coy suggested that the dithionylphosphate ion disproportionates to form dithionylphosphorodithionate (which they observed with ^{31}P -NMR) and the monothionyl species, and the latter then oligomerises to form the polyphosphate glass (49). Two alternatives are (i) that thionyl groups are hydrolysed by water, either before or after oligomerisation or (ii) that an ultraphosphate network glass is formed initially, which requires two SR groups to be lost in its formation, to give a P:O ratio close to 1:2 (see Appendix A), and that this glass subsequently reacts with metal oxide to form linear polyphosphates.

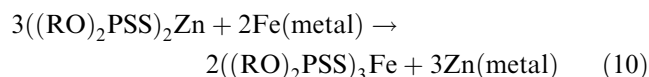
Hilgetag and Teichmann point out that all of the above reactions stem from the fact that the thiophosphoryl sulphur is a weak base which bonds preferentially to weak acids such as tetrahedral carbon and sub-group B metals, while oxygen is a hard base which reacts mainly with hard acids such as protons and phosphoryl phosphorus [126]. Thus the whole set of reactions of the mono and dithiophosphates are effectively aimed at replacing P–S, P=S and C–O bonds by C–S bonds (and thus mercaptans, sulphides and disulphides) and P–O and P=O bonds (and thus polyphosphates). Thus the chemical literature confirms and explains what is seen when ZDDPs are heated in mineral oil at temperatures over 150 °C, the formation of polyphosphates and organic sulphides. In their paper, Jones and Coy also showed how the relative thermal stabilities of the straight and branched chain primary and the secondary ZDDPs were precisely as expected from the above reaction mechanism [49].

The question that clearly follows is whether this same reaction scheme is responsible for the thermal and tribo-films formed by ZDDPs on metal surfaces. This will be discussed in sections 4.6 and 4.7 below.

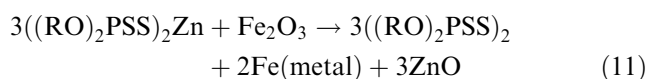
4.5. ZDDP adsorption behaviour

Unless we consider that ZDDP films form by precipitation from solution, the first stage in any surface film formation must be diffusion and adsorption of ZDDP molecules or other moieties on the metal surface. Studies have shown that ZDDP molecules adsorb on iron via the sulphur atom of the P=S bond [114]. As the temperature is raised above about 60 °C, a very striking loss of Zn ions occurs and the adsorption then becomes irreversible [58]. This is suggestive of the formation of either iron dithiophosphate (via cation exchange with iron oxide) or hydrolysis by surface water or hydroxides to give the free dithiophosphoric acid. (Although the latter is a strong acid and thus would probably immediately react with Fe₂O₃ to form the iron salt [21]).

Homann *et al.* [127] studied the reaction of ZDDP in hexadecane solution with both oxidised and reduced iron and nickel metal surfaces. With reduced iron and nickel they noted the redox reaction, e.g.



while with iron and nickel oxides, both an ion exchange and a redox process were noted. In the latter, the authors suggested that the ZDDP was oxidised to the disulphide while the metal oxide was reduced to metal.



Whether ZDDP is the principle adsorbing species in the formation of thermal or tribofilms is not yet clear. As far back as 1958, Larson found that the decomposition products of ZDDP formed at 178 °C were effective in forming surface films that prevented bearing corrosion [14], while much more recently Fuller *et al.* have suggested that the O/S exchange isomer also adsorbs on steel surfaces [91] and have conjectured that ZDDP reaction films are produced via adsorption and reaction of this species rather than direct ZDDP reaction. This is further discussed in section 5.2 below.

4.6. ZDDP thermal film formation

When steel, copper and a number of other metals are immersed in heated ZDDP solution at temperatures above about 100 °C, transparent, solid, reaction films form on the metal surface. These “thermal films” have similar composition to tribofilms, consisting mainly of a thin, outer layer of polyphosphate (≈ 10 nm thick) grading to pyro- or orthophosphate in the bulk [41,89]. Unlike tribofilms, ZDDP thermal films on iron show little evidence of iron in the film itself, the main cation being zinc [77].

The rate of thermal film formation increases with temperature and films can reach at least 200 nm thickness on steel surfaces [91] and recently, films up to 400 nm thick have been reported on gold surfaces at 200 °C [84]. Rubbing experiments on thermally formed films have shown that they are quite resistant to wear, surviving for at least 12 h when rubbed in base oil [89]. Unlike tribofilms, little work has looked at the morphology of thermal films, especially those formed well below the ZDDP decomposition temperature. They appear to grow as separate islands to form a mound-like structure which subsequently coalesce to form, at least at high temperatures, a smoother structure. The most recent published study measured a ZDDP thermal film to have an indentation modulus of $E^* = 35$ GPa and hardness of $H = 1.5$ GPa [83].

A key question of interest is the chemical mechanism by which thermal films form, whether they do so by the S/O exchange and SR displacement mechanism believed to occur in thermal degradation (equations 7 and 9 above) and if so where this reaction takes place? One complication is that several studies have examined thermal films formed on immersed metals in ZDDP solution at very high temperatures (up to 200 °C), so close to the thermal decomposition temperature of many ZDDPs that is difficult to distinguish any surface-specific thermal reaction from the bulk degradation

reactions described in the previous section. Based on such high temperatures work, it has, indeed, been suggested that a main mechanism of thermal film formation may involve deposition on metal surfaces of thermal degradation material from the liquid phase [91,84].

However ZDDP thermal films also form at temperatures considerably below the decomposition temperature of the ZDDP without any significant observable degradation in the liquid phase [91,104] and on some metal surfaces in preference to others (and hardly at all on glass). Thus a specific chemical reaction by adsorbed species at metal surfaces seems most likely and, indeed, might be expected for two reasons. Firstly, iron and other metal oxides are Lewis acids and should thus catalyse the thermal degradation reaction. Secondly, the zinc in ZDDP is known to exchange with other available metal ions including iron, to form dithiophosphates

which are significantly less thermally stable than ZDDP itself [31].

Some confirmation that thermal film formation may involve a reaction mechanism similar to that described in the previous section comes from XANES work by Fuller *et al.* [91] where the O/S exchange isomer formed in equation 7 was tentatively identified on steel surfaces immersed in pre-heated ZDDP solution. Unfortunately no pure thionyl phosphates appear yet to have been studied using XANES to confirm this identification. Overall it seems quite likely that thermal films form on metal surfaces by the S/O exchange mechanism described by Jones and Coy, but it must be stressed that the evidence to date is still indirect. To resolve this, some form of *in situ* analysis able to identify the reaction intermediates at surfaces is needed to verify the chemical mechanism of formation of thermal films, as will be discussed later in this paper.

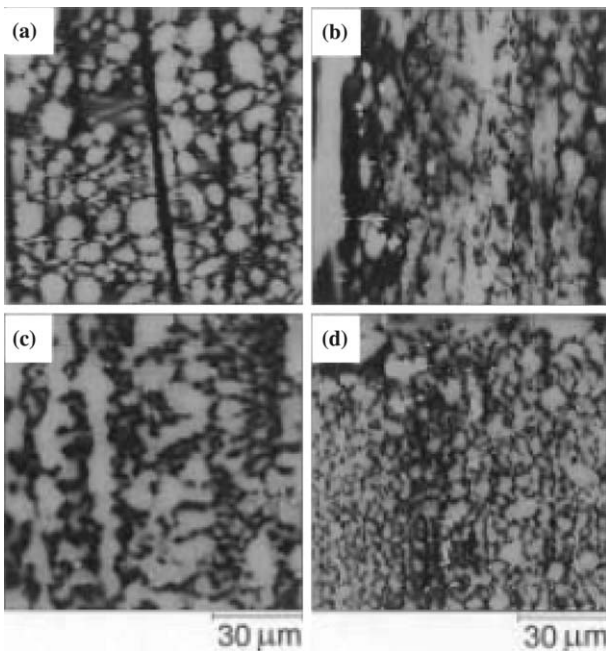


Figure 13. Evolution of pad-like structure of ZDDP tribofilms using AFM. Reprinted from Tribology Letters Vol. 12, Aktary, M., McDermott, M.T. and McAlpine, G.A., Morphology and nanomechanical properties of ZDDP antiwear films as a function of tribological contact time, pp. 155–162, copyright 2002, with permission from Kluwer Academic/Plenum Publishers.

4.7. ZDDP tribofilm formation and properties

In recent years, most academic research activity on ZDDPs has focussed on the nature of the tribofilms that they form on steel surfaces. In consequence we now know a considerable amount about their composition and structure. Below are listed some of our more definite knowledge of the nature of ZDDP tribofilms.

- (i) ZDDP tribofilms form at much lower temperatures than thermal films, even, albeit slowly, at room temperature (in the results shown in figure 5 the test temperature was 50 °C). The rate of film formation increases with increasing temperature [105].
- (ii) These tribofilms form only on the rubbing tracks [16,101,104].
- (iii) They only form if actual sliding contact occurs—they do not develop in rolling contact or if the hydrodynamic film thickness is significantly greater than the surface roughness [104].
- (iv) They have similar chemical composition to thermal films, but are mechanically stronger [89–91].
- (v) They tend to grow to a thickness of about 50–150 nm on steel surfaces and then stabilise at this level [54,94,105].

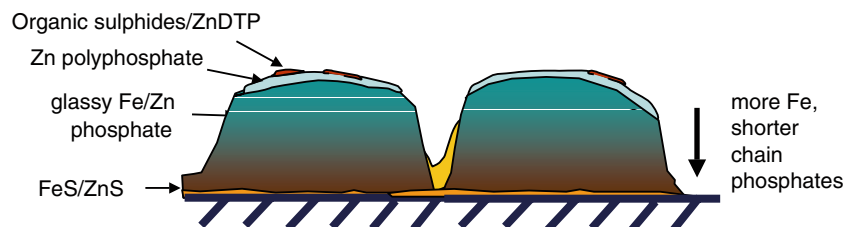


Figure 14. Schematic diagram of pad structure and composition.

- (vi) They initially form as separate patches on steel surfaces and these gradually develop to form an almost continuous, but still pad-like, structure (separated by deep valleys). Figure 13 shows the evolving pad structure measured using AFM [83].
- (vii) The pads consist mainly of glassy phosphate, with a thin, outer layer of zinc polyphosphate [≈ 10 nm thick) grading to pyro- or ortho-phosphate in the bulk [88,95] (see Appendix A). The outer parts of the pad have mainly Zn cations but there is an increasingly large proportion of Fe towards the metal surface [95].
- (viii) Within the pads there is negligible thiophosphate [87,90] but sulphur is present as zinc sulphide [97].
- (ix) On the metal surface below these pads there may be a sulphur-rich layer of zinc or iron sulphide [73,85] although this has recently been disputed by Martin *et al.* [95].
- (x) Basic ZDDPs form very similar tribofilms to neutral salts but with shorter polyphosphate chains in the tribofilm [93].

From recent AFM and nanoindentation studies we also know a good deal about the mechanical properties of ZDDP tribofilms. The pads are solid-like, at least up to 150 °C and most recent work suggests that they have an indentation modulus, E^* of 90 GPa and a hardness, H of 3.5 GPa when probed at room temperature. One curious and not yet confirmed observation is that the pads are “smart” in the sense that they seem to become harder and stiffer during nanoindentation [85]. The origin of this has not been explained but one, as yet unexplored, possibility is that the cores of the pads may contain residual compressive stress (resulting perhaps from conversion of polyphosphate to ortho- and pyro-phosphate, which have lower density).

Figure 14 shows a schematic diagram of the ZDDP tribofilm pad structure. It is important to note that in this, as in similar diagrams in the literature, the scale normal to the surface is about 100 times larger than the horizontal scale. Thus to illustrate their real proportions, the pads in figure 14 should really be only 1/100th of the height shown.

Despite all of the above information about composition, properties and structure, we still have surprisingly little definite information about the mechanism of formation of ZDDP tribofilms, although there have been many conjectures e.g., [91,92,124,128,129]. The main problem is that almost all published research has so far been based on inferring the film formation mechanism from the nature of the film formed or by analogy with thermal decomposition or hydrolysis mechanisms. There is practically no direct knowledge of the chemical intermediates formed at the surface during film formation in a ZDDP-lubricated rubbing contact or, indeed, is it clear whether the reaction is

driven by a tribomechanical, a tribothermal or a tribo-pressure process. This limitation will be further discussed in section 5.1.

4.8. Antiwear properties of ZDDP

When considering the mechanisms by which ZDDP prevents wear, it is important to note that ZDDP is both an antiwear and a mild EP additive, i.e. it both reduces wear and also inhibits the onset of scuffing. This was recognised in the 1960s, when the influence of metal type and alkyl group structure on wear and EP behaviour were measured and compared [35,36]. Antiwear effectiveness was found to correlate inversely with thermal stability of the ZDDP but this trend was less clear-cut with respect to EP effectiveness [35]. Several studies have suggested that the antiwear behaviour of ZDDP results from its ability to form a phosphate film while its EP response results from its ability to form iron sulphide [53,130]. This is consistent with other antiwear and EP additives; sulphur-free phosphorus additives are often effective antiwear but generally ineffective EP additives, while organic sulphides, although possessing some wear-reducing capability are generally regarded as EP additives [131,132]. Similarly, studies have shown that in mild rubbing conditions the surface film present is mainly a thick phosphate film but that in severe, heavily loaded/high sliding speed conditions a much thinner film with high sulphur content is formed [53]. Thus we need to distinguish between the “mild-wear” and “severe wear” action of ZDDP, the latter being essentially an EP response. This EP aspect will not be discussed in detail in this review except to note that studies of thermal degradation of ZDDP have shown that most of the sulphur present in these molecules is converted to oil-soluble organic sulphides and disulphides and that these are well-known EP additives.

From the literature, three main ways that ZDDP acts as an antiwear agent have been proposed; (i) by forming a mechanically protective film; (ii) by removing corrosive peroxides or peroxy-radicals; (iii) by “digesting” hard and thus abrasive iron oxide particles. Each of these is discussed briefly below.

The most generally accepted view of ZDDP antiwear action is that the reaction film acts simply as a mechanically protective barrier [133]. This prevents direct contact and thus adhesion between metal or metal oxide surfaces and may also operate as a cushion, reduces the stresses experienced by the asperity peaks of the metal substrate. The relative importance of these two effects has not been determined. With this type of antiwear action, once a ZDDP film forms, practically all that wear that subsequently occurs is presumed to be that of the ZDDP film itself. (In fact, ZDDP tribofilms appear to be very resistant to wear and several studies have shown that once formed they

are only very slowly worn away even when the ZDDP-containing oil is replaced by a base oil [89,103]). In this case, in mild wear conditions, the only loss of substrate may be from iron oxide which has reacted to form a phosphate film.

The second proposed mechanism of the antiwear action of ZDDP is that it reacts with peroxides in the lubricant; thereby preventing these from corrosively wearing the metal surfaces present [69,70]. This mechanism was convincingly demonstrated by both Habeeb and Rounds in the 1980s and no subsequent work has challenged it.

The third suggestion is more controversial. Martin and colleagues have proposed that iron oxide particles, that would cause abrasive wear, embed in the ZDDP antiwear film and are “digested” to form relatively soft iron phosphate, thus negating their harmful pro-wear effect [62,64,129]. This model appears to have been inferred from identification of iron phosphate in wear particles and in the rubbing track rather than any direct evidence of iron particle digestion. It does seem likely that iron oxide from the metal substrate diffuses into the ZDDP reaction film to replace some of the zinc cations with iron ones and form iron phosphates, and recently SIMS depth profiling has been used to show that there is a much lower iron oxide concentration beneath the ZDDP tribofilm that on the surrounding metal surfaces [96]. What is lacking as yet is direct evidence that harmful iron wear particles are removed by a digestion process.

One interesting aspect of ZDDP wear performance that has arisen very recently is that ZDDPs appear to strongly promote micropitting wear. Micropitting results from localised plastic deformation due to the surface loadings resulting from rolling/sliding asperity contact and it has been shown that ZDDP, because it very rapidly forms a protective film, prevents or postpones effective running-in of rough surfaces. This leads

to high asperity stresses being maintained and consequent micropitting [134]. What is not yet clear is the extent to which this is an undesirable feature of all antiwear additives or of ZDDPs in particular.

4.9. Friction properties of ZDDP films

The final topic in this discussion of our current understanding of ZDDP behaviour concerns the influence of ZDDPs on friction. When engine fuel economy became an important issue in the 1980s, lubricant formulators soon noted that some ZDDPs had a deleterious effect on engine friction and thus fuel economy [135]. At first it was supposed that this originated from the ZDDP film possessing high boundary friction, but it later became clear that ZDDPs increase friction primarily in mixed lubrication [136]. This is shown in figure 15, which plots measured friction coefficient versus entrainment speed (Stribeck curves) from a rolling/sliding steel ball on steel flat contact lubricated with a ZDDP-containing oil at 100 °C [137]. A series of plots are shown at different stages in a rubbing test, and it can be seen that the main effect of ZDDP is not to increase the boundary friction coefficient at very low speeds, but rather to shift the whole Stribeck curve to the right, so that the contact remains in boundary and mixed friction up to much higher speed than without ZDDP.

Initially it was proposed that this effect originated from the fact that ZDDP reaction films are rough (because of their pad-like structure), as found almost 50 years ago by Bennett [20], so that a higher speed is needed to generate a full separating fluid film than in the absence of a ZDDP film [101,137]. However it has recently been shown that even smooth ZDDP films give increased friction in mixed lubrication [138,139]. It appears that the presence of a ZDDP reaction film on the surfaces somehow inhibits fluid film entrainment compared to bare metal. One possible reason is that the liquid lubricant may slip against the ZDDP pad surfaces, which are extremely smooth [82] and coated with a polyphosphate chain material, and thus not be entrained into the rubbing contact. Liquid slip against very smooth surfaces coated with a grafted polymer layer has been observed experimentally [140].

Although the high friction properties of ZDDP films are generally undesirable, it should be noted that in some applications, such as in continuously variable ratio transmissions, high friction is a sought-after feature and ZDDPs are used to provide this [141].

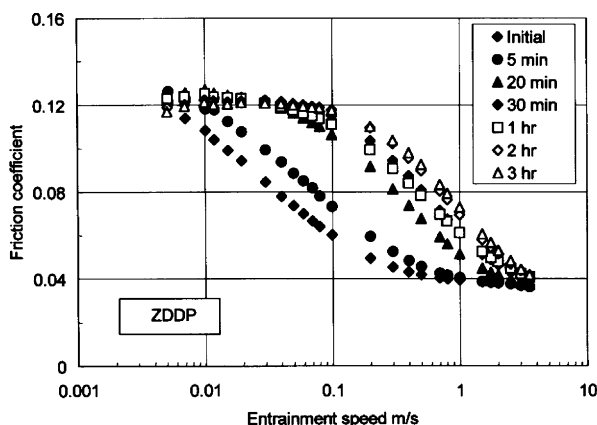


Figure 15. Evolution of friction coefficient behaviour with rubbing time for ZDDP-containing lubricant [137].

5. Outstanding issues

From the above it should be evident that we now know a great deal about what ZDDP additives do in

solution, what they form on metal surfaces and how these reduce wear. However there remain several very important outstanding issues which are still unresolved, a few of which are discussed below.

5.1. Mechanism of formation of tribofilms

Arguably the most interesting unresolved issue in ZDDP antiwear behaviour is the chemical mechanism of formation of the tribofilm. Is it the same thermal degradation process as found at high temperatures in bulk solution, but driven to take place at much lower temperature by cation exchange, frictional heating due to sliding and/or pressure in the rubbing contact? Or is it driven by the rubbing process itself—by molecular strain, exoelectron or other particle emission or free surface catalysis? If the former, then the O/S exchange mechanism known to occur in bulk solution at high temperatures is most likely but if the latter then a radical-based mechanism based on a negative ion process or homolytic bond scission is possible.

Several authors have considered whether the temperature rise in a sliding contact is sufficient to induce ZDDP thermal degradation. Rounds concluded that it was [34], but Georges, who studied lower sliding speed contact, reached the opposite conclusion [142]. The whole question has been recently discussed by Fujita *et al.* who conclude, based on tests conducted at different sliding speeds, that thermal action alone cannot explain the kinetics of ZDDP tribofilm formation and that the existence of some form of surface catalysis that arises during rubbing must be invoked to explain the observed behaviour [104].

So far there is no direct evidence that the O/S exchange reaction takes place in tribofilm formation. Fuller *et al.* found that the compound formed by ZDDP in heated solution that they identified as an O/S exchange isomer was able to adsorb on steel surfaces [91], suggesting that if this isomer is formed during rubbing, it might accumulate at the surfaces. However Taylor *et al.* showed that there was no significant difference in the rates of antiwear film build up between trialkyl phosphate $(RO)_3PO$ and trialkylthiophosphate, $(RO)_3PS$, suggesting that no particular benefit accrued from the presence of the $P=S$ bond and thus easy transalkylation [102].

Probably the only way to resolve this question is to carry out in-contact analysis, and thus observe the chemical intermediates present within the rubbing contact. Vibrational spectroscopy and in particular Raman, which is sensitive to sulphur bonds, may be the most promising approach.

5.2. The reacting species

A closely related question to the one above is the true nature of the chemical species that adsorbs on metal sur-

faces and which subsequently forms thermal and tribofilms. Is it the ZDDP molecules itself, the free dithiolic acid or some other molecule? It is a common observation in the literature that impure ZDDPs often appear to work better than purified ones and, in the 1970s, it was suggested that polar impurities in ZDDP control antiwear film formation [143]. However this is belied by studies that have generated tribofilms using purified ZDDPs at very low temperatures, where solution reaction of ZDDP to form reactive intermediates is unlikely.

There is certainly evidence to suggest that film formation by ZDDPs at high temperatures may involve a breakdown product of ZDDP rather than the molecule itself. As far back as 1958, Larson found that the decomposition products of ZDDP formed at 178 °C were effective in forming surface films to prevent bearing corrosion [14]. This has been supported by recent work, which has shown that solutions in which ZDDP has been almost fully thermally degraded at high temperature still continue to be able to form thermal and tribofilms [91].

It is still not clear whether a significant amount of ZDDP additives survives during a full oil drain interval in engines and thus continue to provide tribofilm formation, but recent studies have indicated that some unreacted ZDDP survives extended engine tests and thus may be available as an active species throughout [144].

5.3. Thick viscous layer

A third outstanding question in ZDDP behaviour concerns the possible presence of a thick, viscous layer of organophosphate material on top of the generally accepted, solid-like, antiwear pads. This concept was first proposed based on cryogenic studies [73,74] and later supported by sliding nanoindentor work by Bec *et al.* who suggested that the solid-like film was covered by a viscous layer of phosphate-rich material up to a micron thick on rubbed surfaces [85]. However in a recent study of elastohydrodynamic film formation by ZDDP-rubbed surfaces, Taylor *et al.* could find no evidence of enhanced fluid entrainment, which would be expected from the presence of a viscous surface layer [139].

There are several possible explanations for this discrepancy. One, which is always prevalent in ZDDP work, is that the types of ZDDP used by the two studies may have been sufficiently different to produce contradictory results. The second is that the viscous film measured by Bec at very low strain rates is highly non-Newtonian and shear thins entirely at the levels of strain rate present in a lubricated contact inlet. A third explanation might lie in experimental differences. In Bec's work, the test specimen studied had been cooled to room temperature and stored for some days after the original rubbing test, so it is not possible to be sure

whether this thick, viscous film was deposited upon cooling and storage or was actually present during rubbing and was thus part of the acting antiwear film. (This reflects a general limitation of AFM and nanoindentation studies to date—that they have all measured the properties of ZDDP films at room temperature rather than at the generally much higher temperatures at which they were formed). In Taylor's work, the rubbed surface was maintained at the test temperature and tested for fluid film entrainment immediately after rubbing.

At present it is not possible to say with any certainty whether a thick viscous layer is present on the ZDDP tribofilm. This is an important question since such a film might be expected to play a significant role in helping separate the rubbing surfaces and thus reduce friction and wear and also, of course may help in understanding how the solid-like tribofilm is generated.

5.4. Tribofilm kinetics

A final, very important area of ZDDP behaviour, about which far too little is known, concerns the kinetics of formation, removal and replenishment, and the role that these play in antiwear performance. This has become an increasingly important issue in recent years, with the need to reduce phosphorus concentration in engine oils and thus to understand the influence of additive concentration both on depletion of ZDDP from solution and the extent to which this limits the effectiveness and survivability of the tribofilm. Some modelling work has already started in terms of tribofilm kinetics but this is so far limited by the paucity of experimental data [145].

Work using interferometry [101–105], ECR [43,44,47] and XANES [94] has studied the rate of film formation and shown that this is dependent on temperature and concentration. Generally, when the ZDDP-containing lubricant has been replaced by a ZDDP-free one, it has been found that the ZDDP tribofilms is worn off only very slowly [89,105]. However a study by Minfray *et al.*, has shown that a ZDDP tribofilm that was etched into narrow transverse strips, was quite rapidly worn off [146]. Recent work also indicates that the presence of other additives such as dispersants may play a key role in the removal of ZDDP tribofilms [105].

6. Conclusions

This paper has reviewed the history of the lubricant additive ZDDP, both in terms of its use and the very large volume of research it has inspired. The main aim has been to show how we have reached our existing state of knowledge about how ZDDP works as a corrosion inhibitor, an oxidation inhibitor and an anti-

wear additive, and to indicate areas where further understanding is still needed.

ZDDPs were first introduced in the late 1930s or early 1940s as oxidation and copper-lead bearing corrosion inhibitors. Their role as an antiwear additives became evident in the 1950s.

ZDDP activity starts in the solution phase where four different reactions can occur (i) ligand exchange, (ii) reaction with peroxides/peroxradicals, (iii) thermal degradation via a O/S exchange, (iv) adsorption at metal surfaces. The functionality of ZDDP is critically dependent on all four of these processes.

In terms of oxidation inhibition, ZDDPs appear to act as metal deactivators both at surfaces and in solution and as peroxide and peroxy-radical decomposers in solution. In the latter two roles, ZDDPs form sulphur-containing species that themselves continue to decompose peroxy-species.

There has been surprisingly little recent published research on the ability of ZDDPs to act as a corrosion inhibitor, although this was once a key role of the additive. ZDDPs form thermally activated reaction films (“thermal films”) on steel and, based on very early work, appear to form similar films on other metals. These thermal films consist primarily of a zinc phosphate glass having a broadly similar composition to the much more heavily researched ZDDP tribofilms.

Most attention in recent years has focussed on the ability of ZDDP to form tribofilms on rubbing iron and steel surfaces under mild wear conditions and, in particular, on the chemical composition and properties of these films. These films form at much lower temperatures than those at which ZDDP normally shows chemical activity. They consist primarily of closely packed pads of glassy, zinc ortho- and pyrophosphate, typically 5 μm across and 100 nm thick. The outermost layers of these pads contain longer chain zinc polyphosphate. The lower layers next to the surface contain some iron cations in place of zinc. Between the pads are fissures containing bulk solution.

The main mechanism by which ZDDPs reduce mild wear is probably by preventing the metal surfaces from contacting one another, and thereby reducing adhesive wear although, under more severe conditions they also act as an EP additive to form metal sulphides and the phosphate glass present may also digest ferric oxide particles to limit abrasion.

Despite the enormous amount of research work carried out over 50 years, there are still several important gaps in our understanding of how ZDDPs work. In academic terms, probably the most significant is our lack of a proven chemical reaction sequence from ZDDP to metal phosphate in the formation of antiwear tribofilms. Many such mechanisms have been

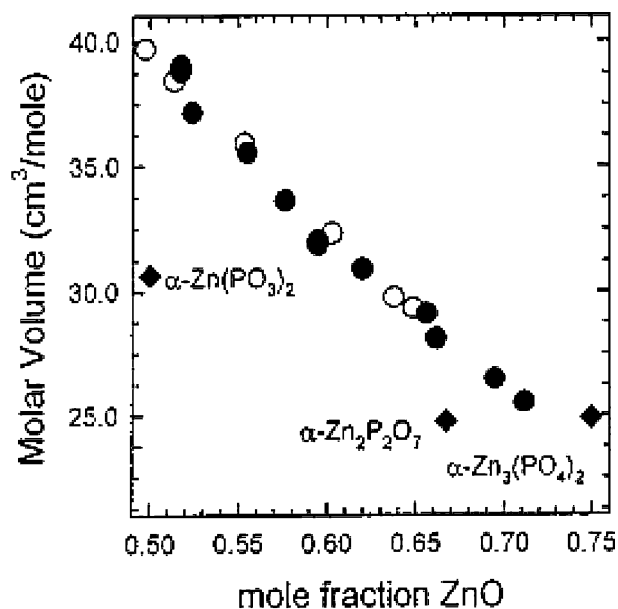


Figure 16. Density of zinc phosphate glasses. Reprinted from J. of Non-Crystalline Solids Vol. 191, Brow, R.K., Tallant, D.R., Myers, S.T., Phifer, C.C., The short-range structure of zinc polyphosphate glass, pp. 45–55, copyright 1995, with permission from Elsevier.

proposed based on the chemical nature of the film formed. However in the absence of direct chemical evidence of intermediate species in and around rubbing contacts, these remain conjecture.

Appendix A. Zinc phosphate glasses

The antiwear properties of ZDDP appear to be very closely related to the ability of ZDDP to form zinc and other metal polyphosphate glasses and this appendix describes the main types of structure formed in such glasses. A review of phosphate glasses including those of zinc has been given by Ray [147] while Brow *et al.* describe ^{31}P NMR, Raman and XPS studies of zinc phosphate glasses and also their refractive index and density characteristics [17,148].

Most zinc phosphate glasses can be made quite easily by melting zinc oxide and acid ammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ together in various proportions at 1000°C and then cooling rapidly to prevent crystallization. Depending on the proportion of ZnO used, the structures are obtained with the following anions matched by the appropriate charge-balancing ratio of Zn^{2+} ions.

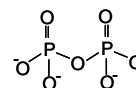
The different glasses that can be formed in this way are shown in the figures below. The anionic charge is balanced by Zn^{2+} ions. (Note that although $\text{P}=\text{O}$ and $\text{P}-\text{O}^-$ bonds are shown separately in these figures, when these occur on the same P atom they are actually

indistinguishable and the charge is shared equally between them).

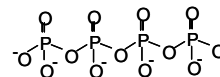
orthophosphate, PO_4^{3-}



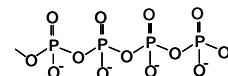
pyrophosphate, $\text{P}_2\text{O}_7^{4-}$



polyphosphate, $\text{O}(\text{PO}_3)_n\text{O}^{(n+2)-}$



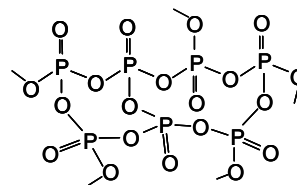
metaphosphate (cyclic), $(\text{PO}_3)_n^{n-}$



The densities of these zinc glasses are shown in figure 16 [17]. (Note that in this figure, the molar volume of the ordinate is the volume of x moles of ZnO and $(1-x)$ moles of P_2O_5 where x is the mole fraction of ZnO on the abscissa). Also in this figure are shown the densities of the crystalline, as opposed to the glassy ortho-, pyro- and metaphosphates. As might be expected these are denser than the glassy phosphates.

In addition to the above, there also exists ultraphosphate glass, which has $\text{P}-\text{O}-\text{P}$ links replacing some of the $\text{P}-\text{O}^-$ anions and thus contains only a very small number of zinc cations as shown below. In the extreme this has the molecular formula $(\text{PO}_2)_n$ and is thus a phosphorus oxide. Ultraphosphate glasses are surprisingly stable to bulk hydrolysis although they form a very thin hydrolysed film on the surfaces, and have low softening temperatures, in the $150\text{--}250^\circ\text{C}$ range. It is not known if such glasses are formed in ZDDP films and their X-ray spectroscopic properties do not appear to have been determined.

Ultraphosphate glass



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