

Fundamental Understanding of Antiwear Mechanisms in Real-World Applications: Part 2

Oliver M. Smith, Nga Nguyen, Ewan Delbridge, James Burrington,
Binbin Guo, Jason Hanthorn, and Yanshi Zhang
Lubrizol Corporation (The)

ABSTRACT

The global commitment to reduce CO₂ emissions drives the automotive industry to create ever more advanced chemical and engineering systems. Better vehicle fuel efficiency is demanded which forces the rapid evolution of the internal combustion engine and its system components. Advancing engine and emission system technology places increasingly complex demands on the lubricant. Additive system development is required to formulate products capable of surpassing these demands and enabling further reductions in greenhouse gas emissions. This paper reports a novel method of generating fundamental structure-performance knowledge with real-world meaning. Traditional antiwear molecule performance mechanisms are explored and compared with the next generation of surface active additive system (SAAS) formulated with only Nitrogen, Oxygen, Carbon and Hydrogen (NOCH). Results of experiments run with the advanced antiwear NOCH SAAS show significant improvements over traditional fully-formulated lubricants through a mechanism that deviates from that of conventional antiwear molecules.

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INTRODUCTION

One of the primary functions of an engine oil is to control engine wear and ultimately increase engine durability. For the last 50 years this has almost exclusively been achieved through application of Zinc Dialkyldithiophosphate (ZDDP), an additive specifically functionalized to perform this task throughout the entire life of an engine lubricant. Modern formulations require reduced levels of both phosphorus and zinc and prompt the re-design of molecules capable of providing increased antiwear performance while composed of only NOCH. The process of developing such molecules relies heavily on a deep fundamental understanding of the structure-performance relationship which is derived from the performance testing process.

Mechanical Properties of ZDDP-Derived Tribofilms

An excellent review of the last 50 years of research covering the history and mechanism of ZDDP is provided by Spikes, which details key information from nearly 150 research papers [1]. Tribofilm formation and properties are covered extensively. It is reported that the ZDDP tribofilm product forms in pad-like structures with a hardness approximating 3.5 GPa when probed with a nanoindenter at room temperature. This hard reaction film acts as a mechanical barrier, preventing direct contact and thus adhesion and abrasion. The result of this action means that once a ZDDP tribofilm is stabilized in a tribocouple, practically all the wear that occurs is likely to be from the film itself, and not the metal substrate. The key drivers for the effectiveness and survivability of the film are not well understood. The kinetics of formation, removal and replenishment can be

influenced by other additives in the solution phase, as well as the phosphorus content itself. As emissions legislation drive the lubricants industry towards lower phosphorus levels in finished lubricants, this understanding becomes more critical. In a review presented by Gellman *et al* it is reported that the challenge for the additive chemist is now the application of this knowledge in the design of improved antiwear additives with greater environmental compatibility [2]. This work provides a review of developments in surface analytical techniques that have led to the comprehensive mechanistic understanding that exists around the mechanisms of ZDDP. Similarly to the Spikes review, the overarching understanding of the structure of ZDDP tribofilms suggests the steel substrate surface to be covered in a thin layer of iron oxides and sulphides, in turn covered by a thin layer of short-chain phosphates which is then covered by a patchy long chain polyphosphate glass material with hardness in the order of GPa. More loosely bound to this surface is a viscous alkylphosphate layer several hundred nanometers thick and with hardness in the order of MPa.

Research reported by Bec *et al.* dives more deeply into the relationship between the mechanical properties and structure of ZDDP tribofilms [3]. The kinetics of film formation and removal are shown to be associated with the appropriate mechanical properties. For good wear resistance, it is reported that an optimal tribofilm must have a high shear strength permitting an adequate rate of formation and maintaining integrity. It should also have sufficiently low shear strength to ensure its shear plane is located within the film itself, thus limiting substrate wear. Wear of the substrate material is suggested to

be dominated by mechanical and/or chemical corrosive interactions between areas of the contacting surfaces that are less well protected by the phosphate layers. Using novel experimental techniques, measurement of the mechanical properties of ZDDP films was possible. The hardness of the near-surface sulfide/oxide layer was found to be 4.7 GPa, while the polyphosphate layer was measured to be in the range of 1 GPa -2 GPa. The conclusion is drawn that the polyphosphate film can be thought of as a truly smart material. It is shown to have a unique ability to respond to a wide range of imposed conditions to provide the required resistance to contact for any given situation. This was founded on results that showed that the hardness of the polyphosphate could increase with applied pressure. The analogy can then be made between the action of the polyphosphate film and a pressure sensor.

Testing for Antiwear Properties

Engine oil additive effects on wear are frequently assessed using tightly controlled laboratory scale apparatus designed to focus on mechanisms believed to be of key importance to the performance of the lubricant. This ethos is covered in extensive detail in Part 1 of this paper series [4]. In work reported by McQueen *et al.*, the treat-rate effect of phosphorous containing lubricants was examined using a ball-on-flat reciprocating tribometer [5]. Wear scars were evaluated on the disc specimen rather than the ball. Results clearly indicated that increasing the level of phosphorus can reduce the wear volume. This was an effect they were able to measure in a motored valvetrain rig equipped with radioactive tracer technology. In this apparatus they were also able to observe the effect of tribocouple hardness on wear. The softer cam lobe wore approximately twice as much as the harder tappet insert. This same technique was able to show that binary systems can produce different results to fully formulated systems, and that in the latter, wear can be appreciably reduced.

The influence of lubricant ageing on tribological performance is something that is more often overlooked in simple lubricant screening work, but has been investigated using a variety of methodologies. De Feo *et al.*, used a ball-on-flat configuration to investigate the influence of a laboratory based oxidative procedure on lubricants containing molybdenum dithiocarbamate (MoDTC) and witnessed increasing surface damage with increasing oxidation, and significant differences in the structure of the tribofilms [6]. A similar effect was reported by Costa and Spikes, but this time not as a function of oxidation, but as a function of lubricant contamination. The presence of ethanol in the lubricant mix was shown to result in less stable tribofilms which were more easily removed and resulted in surface damage [7]. Soot containing contamination has also been shown to influence the wear performance of a system. Experiments conducted by Kontou *et al.* were able to show that ZDDP films formed by fresh lubricant were rapidly removed after the addition of carbon black, which was induced to simulate soot contamination [8]. The relationship between soot surface chemistry and wear is well explored by Uy *et al.*, who reported that differences in the exact soot type can influence the wear mechanism itself [9]. An alternative to creating oils simulative of degradation is to tribologically measure the performance of drain samples taken from fired engine tests. Konicek *et al.* report that using ball-on-flat testing on periodic samples from a sequence IIIG test they

were able to demonstrate that the oil did produce a thinner tribofilm, suggesting that it is possible that in the early stages of an engine test, a tribofilm was formed and wore away as the lubricant aged [10].

There are a vast number of variables that can have an effect on the antiwear performance of a lubricant. Experiments to screen performance and guide the development of molecules to reduce wear must be carefully designed to provide results with any real-world meaning. This research reports a novel experimental methodology designed to do just that. The experiment is used to show that mechanistic understanding of antiwear system can complement results from novel surface analyses techniques reported in the literature. The unique abilities and mechanism of action of a NOCH SAAS formulation is explored and shown to enable superior antiwear performance with dramatically reduced phosphorus levels.

METHOD

The following methodology was designed to create an accelerated screener test, whilst incorporating the key drivers thought to influence wear in the fired engine sequence IVA wear test. The detailed reasoning behind the test structure is provided in part 1 of this publication [4]. Essentially the methodology is designed with two key phases that are thought to dominate in the engine test.

1. Tribofilm formation phase: a robust tribofilm forms as quickly as possible, protecting the surfaces from metal-metal contact under the prescribed 'fresh oil' conditions.
2. Antiwear durability phase: The pre-formed and stable tribofilm continues to attempt to protect the surfaces and replenish/repair during the presence of superincumbent contaminants. This 'attack' results in localized or total removal of the tribofilm giving rise to accelerated wear.

The 2-phase approach is illustrated in Figure 1.

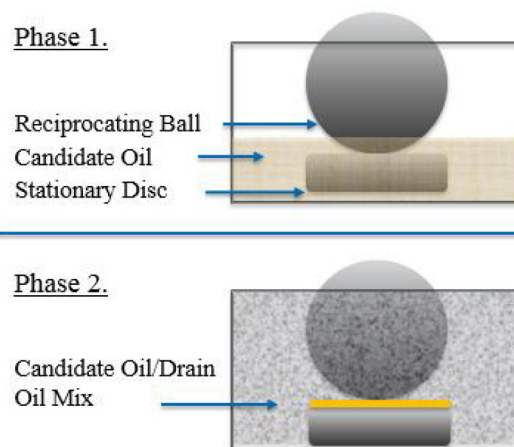


Figure 1. Schematic representation of the 2-phase method.

The test was run on a PCS Instruments High Frequency Reciprocating Rig at isothermal conditions of 120 °C. This temperature was chosen to ensure all testing was conducted in the boundary lubrication regime only. A load of 200 g was applied with a 6 mm diameter 52100 steel ball of RC 58-66 and surface finish of