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Role of zinc dialkyl dithiophosphate in carbon black induced abrasive wear

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ABSTRACT

We have explored the contact conditions under which zinc dialkyl dithiophosphate (ZDDP) is corrosive and, in the presence of carbon black, increases wear. It was found that the corrosivity of ZDDP to steel is due to a load dependent mechanochemical reaction and leads to the antagonism between ZDDP and carbon black which is also likely to be load dependent. Depth-profiled Auger spectroscopic analysis of wear scars produced with ZDDP shows that the iron sulfide layer thickness depends on contact load during the wear process. Higher loading produces a thicker iron sulfide layer but, surprisingly, the thickness is relatively insensitive to time. Indenter nanoscratching measurements demonstrate that the highly corroded surface is less scratch resistant than lightly corroded surfaces made under lower load (or of the native steel), explaining increased wear by abrasion of carbon particles (*e.g.* carbon black or soot) under highly loaded conditions.

1. Introduction

Lubricants are designed to reduce wear and friction under a wide range of conditions and applications. The most common antiwear additive used in engine lubricants is zinc dialkyl dithiophosphate (ZDDP) because of its effectiveness in a variety of hardware under a wide range of operating conditions. For example, ZDDP is used in lubricants for light duty gasoline and diesel engines. ZDDP is also used in large heavy duty diesel engines which are exposed to soot produced by the combustion process. Soot can be abrasive and increase engine wear severity [1]. Heavy duty diesel engines usually undergo longer oil drain intervals than light duty gasoline engines which contribute to the high end-of-oil-life concentration of contaminants and soot.

The mechanism of ZDDP antiwear activity has been extensively studied [2–5] and it is generally believed that additive effectiveness is related to its ability to transform into a protective film during mechanical contact between rubbing surfaces. This protective *tribofilm* can grow to be hundreds of nanometers thick [6], consisting of a complex phosphate structure [7], and only forms within the area exposed to both high temperature and mechanical rubbing. Contact pressure [8,9], among other factors, has been shown to significantly impact tribofilm structure, if one forms [10].

Recent work has suggested that the antiwear performance of ZDDP may be compromised in the presence of soot. The Spikes group [11,12] has proposed that, under some conditions, ZDDP can corrode a ferrous surface and expose the surface to increased abrasive wear in the presence of a laboratory surrogate for soot, carbon black. Recent research [13] has confirmed that the antagonism between ZDDP and soot is caused by a corrosive-abrasive wear mechanism. Others have shown that under high load ZDDP can corrode steel to form iron sulfide [14]. The antagonism between ZDDP and carbon black has important implications for highly-sooted, heavy duty diesel lubricants and further research is needed to understand the nature of any antagonism between soot and ZDDP and under what conditions it occurs. Smaller, higher output engines with high contact pressures and high levels of soot can potentially further stress engine durability. Consequently, the performance of ZDDP in the presence of soot is a question of great practical relevance. In this work we show that the corrosivity of ZDDP is dependent on contact conditions and directly measure the mechanical properties of the triboproduct produced by ZDDP in the wear contact.

2. Experimental

2.1. Test lubricants

Two formulated lubricants were used in this work: (1) a commercial lubricant with a full complement of performance additives, and (2) that same commercial lubricant with ZDDP and friction modifier additives removed. Sliding wear tests were run on these two lubricants after adding 4.8 wt% carbon black (Monarch 280). This level of soot was considered to be representative of a sooted lubricant. Lubricants were homogenized with an acoustic

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horn to fully disperse the carbon black. All other wear tests were run on the as-is ZDDP additive (commercially available as Lubrizol 1371).

2.2. Sliding tests

Sliding tests were conducted using a high frequency reciprocating rig (HFRR, PCS Instruments) ball-on-flat tribometer. Operating conditions were 10 Hz frequency, 100 °C temperature, and 2.0 mm wear scar length. The contact loads and total test durations were varied for each test as described below. The ball was held in a fixed position by a set screw to prevent rolling. Test lubricant temperatures were equilibrated for 15 min before sliding began. The stainless steel ball and sample disc were standard 52100 bearing steel, with nominal hardness values of 200 HV30 for the disc and 62 Rockwell C hardness for the ball. These are standard specimen sets used in the HFRR, where the ball is made harder in order to induce wear primarily on the disc. Testing and subsequent wear measurements were performed on the as-received polished side of the HFRR discs.

Wear was calculated on the discs using data from a Dektak stylus profilometer (Veeco Dektak 150). Depth profiles were made perpendicular to the direction of rubbing in three different locations along the wear scar. The depths of each profile near the middle of each scan were averaged to quantify wear.

2.3. Auger electron spectroscopy

Wear scar surfaces were analyzed for elemental composition using Auger electron spectroscopy (AES) after rinsing samples in heptane to remove lubricant residue. A Physical Electronics model 680 scanning Auger microprobe was used with a 10 keV beam voltage and beam current of 10 nA. Sputtering was accomplished with a 4 keV argon ion beam and a current of 2.0 μA. The sputter rate was calibrated on SiO_2 to be 185 Angstroms per minute. All surface composition measurements were taken after briefly sputtering off the top 2.5 nm of the surface to remove adsorbed impurities. We have found that surface contamination due to atmospheric impurities is impossible to prevent with samples prepared outside of a vacuum chamber. Consequently, with highly surface sensitive methods such as AES, it is important to remove the first couple of nanometers before quantitative surface analysis.

AES has the advantages of both high surface sensitivity and high spatial resolution. As such, a focused electron beam can be used to produce two-dimensional elemental maps that show the composition of the contact surface. This is especially useful when analyzing compositionally heterogeneous wear scars. Between sputtering depth profile steps, average elemental composition was measured using a defocused beam to account for heterogeneities in the wear scar surface. AES is generally sensitive to elements which are present at concentrations at or above 1%. Consequently, data for elements present at trace level are not reported here.

2.4. Scratch tests

Scratch tests were conducted with a Hysitron TriboIndenter with a cono-spherical tip of 1 μm radius. The indenter applies a normal load on the sample surface as it moves a prescribed lateral distance. The user defines a load function, along with the lateral displacement, as a function of time. Two outputs are recorded during a scratch test: normal displacement into the surface, and lateral force (friction) experienced by the indenter tip for the input load function. A constant maximum load function was used for these experiments.

Sample roughness can impact the scratching measurement. Consequently, relatively smooth areas were selected for scratching experiments. In addition, the load function was set up to account for roughness by first moving the indenter tip over the entire scratch distance with a low load (2 μN) to survey the surface and record the initial topography as a starting reference. Then the scratching load was applied while again going through the entire scratch length. The normal displacement recorded by the indenter before the actual scratching was subtracted from the normal displacement of the indenter when the full load was applied to give the depth of scratch for a specific load function. The nanoindenter loads applied for tribofilm scratching experiments were 50 μN, 100 μN, 200 μN, and 400 μN. The scratch lengths were 0.5 μm.

3. Results

The antagonism between ZDDP and carbon black was confirmed by testing the two lubricants described above in the HFRR using a static load of 400 g for 2 h. One wear test was performed with the lubricant containing the full commercial formulation including ZDDP, friction modifier, and carbon black, and another wear test was performed with the lubricant containing carbon black in the same formulation, but without ZDDP or friction modifier. The wear scar created with ZDDP had a depth of 1.25 μm compared to the scar made without ZDDP which had a depth of 0.5 μm. Optical images of the two wear scars (Fig. 1) show that both have the striations in the direction of motion indicating an abrasive wear mode, likely from the soot. The images also demonstrate that the ZDDP containing lubricant produced a substantially wider wear scar.

To further explore the nature of this antagonism, HFRR wear tests were run on concentrated, as supplied, ZDDP. Concentrated ZDDP was used instead of a dilute lubricant blend to enhance mechanically-activated tribochemistry and provide a sufficiently thick layer of triboproducts to enable further analysis of their mechanical properties. As will be discussed below, reliable nanoindenter measurements require a relatively thick film. Fig. 2 shows surface AES elemental maps for the wear scar made with a 400 g load in the neat ZDDP additive. The field of view shows the elliptical wear scar end at an angle. The elemental maps illustrate that inside the wear scar sulfur is highly concentrated and that iron and oxygen are the other predominant elements. Fig. 3a is the elemental depth profile for this wear scar. Iron and sulfur remain primary components through the entire depth profile which shows elemental composition inside the wear scar down to a depth of 400 nm. Sulfur is likely present primarily as iron sulfide since the concentration of zinc and phosphorous is too low for a

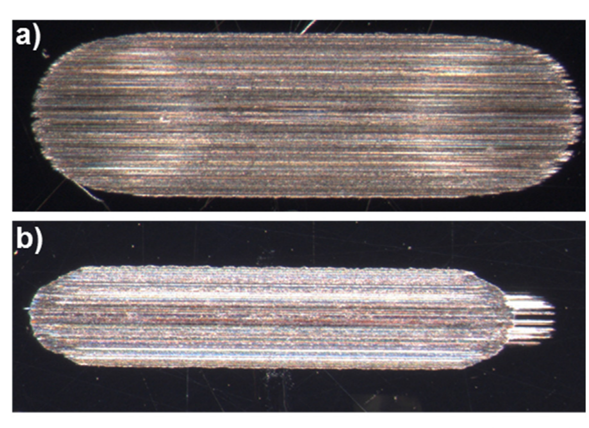

Fig. 1. Optical images of wear scars made with (a) full lubricant formulation and carbon black, and (b) the same formulation as (a) but with antiwear and friction modifier removed. Scale bar is 200 μm.