Zinc dialkyldithiophosphates operate mainly as antiwear agents but exhibit mild extreme-pressure characteristics. As an antiwear agent, ZDDP operates under mixed lubrication conditions with a thin oil film separating the metal parts. Surface asperities, however, intermittently penetrate the liquid film, giving rise to metal-on-metal contact. The ZDDP reacts with these asperities to reduce this contact. Likewise, when the load is high enough that the oil film collapses, the ZDDP reacts with the entire metal surface to prevent welding and reduce wear. A great deal of study has been done to determine the nature of this protective film and the mechanism of deposition, where the thermal degradation products of the ZDDP are the active antiwear agents.

The antiwear film thickness and composition are directly related to temperature and the extent of surface rubbing. Initially, ZDDP is reversibly absorbed onto the metal surface at low temperatures. As the temperature increases, catalytic decomposition of ZDDP to dialkyldithiophosphoryl disulfide occurs, with the disulfide absorbed onto the metal surface. From here, the thermal degradation products (as described in Section 3) are formed with increasing temperature and pressure until a film is formed on the surface [16]. The thickness and composition of this film have been studied using many different analytical techniques, but no one analysis gives a concise description of the film size and composition for the various kinds of metal-to-metal contact found in industrial and automotive lubrication regimes. In general, the antiwear/extreme-pressure ZDDP film can be said to be composed of various layers of ZDDP degradation products. Some of these degradation products are reacted with the metal making up the lubricated surface. The composition of the layers is temperature-dependent.

The first process that takes place is the reaction of sulfur (from the ZDDP thermal degradation products) with the exposed metal leading to the formation of a thin iron sulfide layer [17]. Next, phosphate reacts to produce an amorphous layer of short-chain ortho- and metaphosphates with minor sulfur incorporation. The phosphate chains become longer toward the surface, with the minimum chain length approaching 20 phosphate units. Some studies have indicated that this region is best described as a phosphate "glass" region in which zinc and iron cations act to stabilize the "glass" structure. At the outermost region of the antiwear film, the phosphate chains contain more and more organic ligands, eventually giving way to a region comprised of organic ZDDP decomposition products and undegraded ZDDP itself. The thickness of the film has been analyzed to be as small as 20 nanometers using ultrathin film interferometry and as large as 1 micron using electrical capacitance [18–21].

Recent work has concluded that, although the rate of the film formation is directly proportional to temperature, a stronger correlation exists between film formation and the extent of metal-to-metal rubbing as quantified by the actual distance that the metal slides during a given test period. The film reaches a maximum thickness at which point a steady state between formation and removal exists, the rate of formation being more temperature-dependent than the rate of removal. It was also found that the ZDDP reaction film has a "solidlike" nature (as opposed to being a highly viscous liquid) due to the lack of a reduction of film thickness observed with time on a static test ball [22].

Another mechanism of wear found to be inhibited by zinc dialkyldithiophosphate is wear produced from the reaction of alkyl hydroperoxides with metal surfaces. It was found that the wear rate of automobile engines cam lobes is directly proportional to alkyl hydroperoxide concentration. The mechanism proposes the direct attack of hydroperoxide (generated via fuel combustion and oil oxidation) on fresh metal, causing the oxidation of an iron atom from a neutral charge state to Fe^{+3} by reaction with three moles of alkyl hydroperoxide as described by reactions (2.25):

$$2\ ROOH + Fe \longrightarrow 2\ RO^{\bullet} + 2\ OH^{-} + Fe^{+2} \quad (2.25)$$

and (2.26):

$$ROOH + Fe^{+2} \longrightarrow RO^{\bullet} + OH^{-} + Fe^{+3} \quad (2.26)$$

The ZDDP and its thermal degradation products neutralize the effect of the hydroperoxides by the mechanism described in reactions (2.20)–(2.23) in Section 5. It was also shown that peroxy and alkoxy radicals were far less aggressive toward metal surfaces than hydroperoxides, indicating that free-radical scavengers, such as hindered phenols, would be ineffective in controlling this kind of engine wear. This may explain why the antiwear performance of ZDDP is directly related to its antioxidation performance in the order of secondary ZDDP > primary ZDDP > aryl ZDDP rather than correlating with the order of thermal stability (aryl > primary > secondary) [23].

A recent study has been conducted to investigate the difference in wear performance between neutral and basic ZDDPs in the Sequence VE engine test. The neutral ZDDP performed better in value train wear protection that the basic ZDDP. The basic salt actually failed the Sequence VE engine test, indicating that using commercial ZDDPs with lower basic salt content may be preferred when limited to a 0.1% maximum phosphorus content (as mandated by the I.L.S.A.C. GF-3 motor oil specification). It was suggested that the increased wear protection by neutral ZDDP could be explained by the superior adsorption of the oligomeric structure of the neutral salt, leading to the formation of longer polyphosphate chains relative to the basic salt [5].

7 APPLICATIONS

Zinc dialkyldithiophosphates are used in engine oils as antiwear and antioxidant agents. Primary and secondary ZDDPs are both used in engine oil formulations, but it has been determined that secondary ZDDPs perform better in cam lobe wear protection than primary ZDDPs. Secondary ZDDPs are generally used when increased extreme-pressure activity is required (i.e., during run-in to protect heavily loaded contacts such as valve trains). Zinc dialkyldithiophosphates are generally used in combination with detergents and dispersants (alkaline earth sulfonate or phenate salts, polyalkenyl succinic amides or Mannich-type dispersants), viscosity index improvers, additional organic antioxidants (hindered phenols, alkyl diphenyl amines), and pour point depressants. A typical lubricant additive package for engine oils can run as high at 25% in treatment level. The International Lubricant Standardization and Approval Committee (ILSAC) has designated its GF-3 engine oil specification to include a maximum limit of 0.1% phosphorus to minimize the engine oil's negative impact on the emissions catalyst. For the GF-4 specification, scheduled to take effect in 2004, the limit may be reduced even further if an acceptable Oil Protection of Emission Systems Test (OPEST II), which would replace the minimum phosphorus requirement, cannot be developed. As a result of this minimum phosphorus requirement, the treatment level for zinc dialkyldithiophosphate in engine oil is limited to about 0.5–1.5%, depending on the alkyl chain length used.

The new challenge to motor oil formulators is in passing the required ILSAC tests while keeping the ZDDP level low. Yamaguchi et al. have shown that the antioxidant effect of ZDDP is significicantly enhanced in API group II base stocks with as much as a 50% increase noted for a basic ZDDP. An increase in antioxidancy was also noted when using ZDDPs in polyol ester [24]. Several studies have also shown that ZDDP oxidation byproducts are ineffective antiwear agents. The use of these base stock effects to extend the oxidation life of the ZDDP may be a suitable method for the formulator to reduce the level of ZDDP needed to accommodate the GF-3 limits.

The synergistic effect between organic molybdenum compounds and ZDDP in wear reduction is currently being studied as a means of lowering phosphorus content in engine oils. In U.S. patent 5,736,491, a molybdenum carboxylate is used with a ZDDP to give a synergistic reduction in friction coefficient by as much as 30%, thus allowing a reduction in total phosphorus content and improved fuel economy [25]. The patent literature has sited other organic molybdenum compounds such as molybdenum dithiocarbamates (MoDTC) and dialkyldithiophosphates (MoDTP) as being useful, synergistic secondary antiwear agents.