Lube-Tech
PUBLISHED BY LUBE: THE EUROPEAN LUBRICANTS INDUSTRY MAGAZINE
No.58 page 1

Development of Organic Ashless Antiwear- Friction Modifier additives

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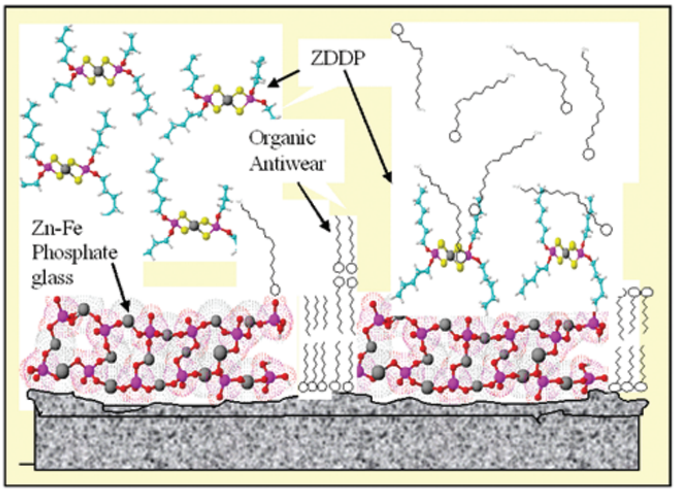
Introduction:

The development of Organic Antiwear/ Friction modifiers (OAW-FM) requires meeting sustained compatibility with the other additives present. Performance from all the individual additives cannot be compromised whether they are antioxidants, detergents, dispersants, viscosity improvers, or other antiwear additives. In particular, the OAW-FM cannot degrade the performance of the zinc-dialkyldithiophosphate (ZDDP) extreme pressure (EP) antiwear additives in fully formulated motor oils. From the engine-emission performance side, the OAW-FM ideally should be free of sulphur and phosphorus, to maintain vehicle pollution control devices.

Since ZDDP, reduces wear at high temperatures and pressures, its surface activity is critical to its performance. Specifically, it must undergo efficiently a transition from a soluble inorganic zinc dialkyldithiophosphate to a protective amorphous zinc-iron phosphate and pyrophosphate glass, at the metal surfaces in contact. This glassy film is sacrificial, and can be both removed and replenished during the engine operation cycle. Effective organic antiwear additives then, must *first: not* compete *with or prevent* the ZDDP from reaching the surfaces, and *second: complement the development of a protective boundary layer films either from ZDDP or the OAW-FM.*

Figure 1.



Schematic representation of the development of Zinc-Iron – polyphosphate films derived from the decomposition of ZDDP at extreme pressure and temperature in the boundary layer lubrication conditions near the piston ring cylinder contact surface.

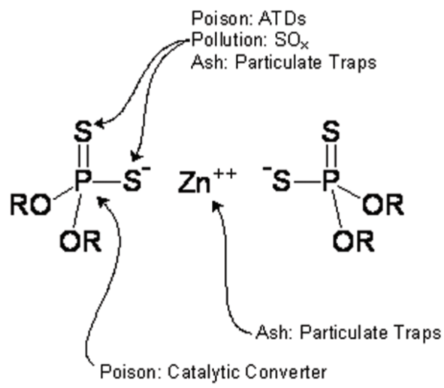
An illustration of this type of surface chemistry dynamics for a three component system, *OAW-FM, ZDDP, and* $Fe_xZn_y(PO_4)_n$ *glass*, is presented in *Figure 1*. This model illustrates the need for a series of mechanisms to establish true cooperative boundary-layer protection. Through a complicated series of equilibria a balance must be maintained between the adsorption and desorption at the *ZDDP-Metal Surface*, the *OAW-Metal Surface*, and between *ZDDP-OAW species*. The kinetics of how these simultaneous adsorption-desorption processes change, can be described by the Langmuir isotherm:

$$\frac{d\theta}{dt} = k_a[A](1-\theta) - k_d(\theta) \quad \textit{for } ZDDP, OAW-FM, Fe_xZn_y(PO_4)_2 \ldots$$

(Where θ = surface coverage fraction, [A] = concentration of additive in solution k_a and k_d are the rate constants for adsorption and desorption respectively, and t = time.)

Since both k_a and k_d have different temperature coefficients, increasing temperature can lead to increased, decreased, or unchanged surface coverage (1). As long as a critical minimum surface film fraction θ = 0.5 is maintained, wear and friction can be controlled. This was described for some specific friction modifiers and antiwear additives including ZDDP (1). Through the careful testing of structure- performance, and compatibility with ZDDP, new organic antiwear additives can be developed. An example of a developed sulphur and phosphorus free additive, synergistic with ZDDP to maintain adequate θ surface film coverage is presented.

Figure 2.



The molecular structure of ZDDP, indicating the elements of detrimental to both the performance of environmental pollution control devices and contributing to SOx, and particulates.