Lube-Tech

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Development of Organic Ashless Antiwear- Friction Modifier additives

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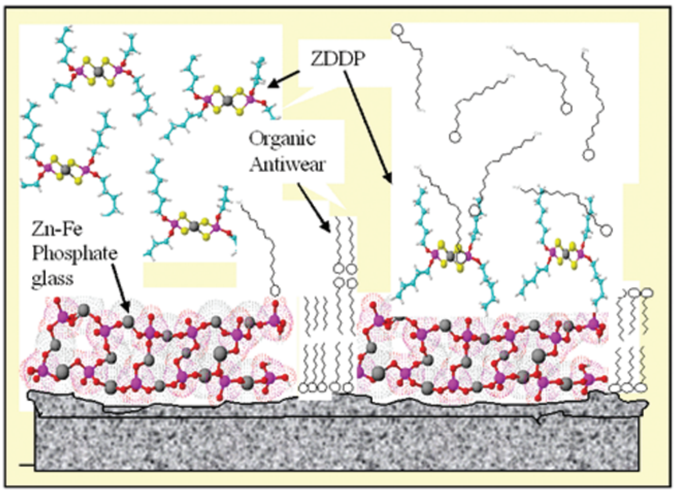
Introduction:

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.

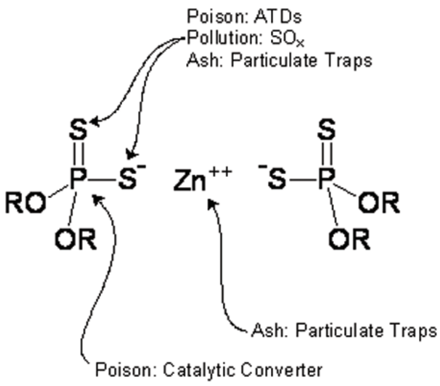
An illustration of this type of surface chemistry dynamics for a three component system, *OAW-FM, ZDDP, and* $Fe_xZn_y(PO_4)_n$ *glass*, is presented in *Figure 1*. This model illustrates the need for a series of mechanisms to establish true cooperative boundary-layer protection. Through a complicated 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.

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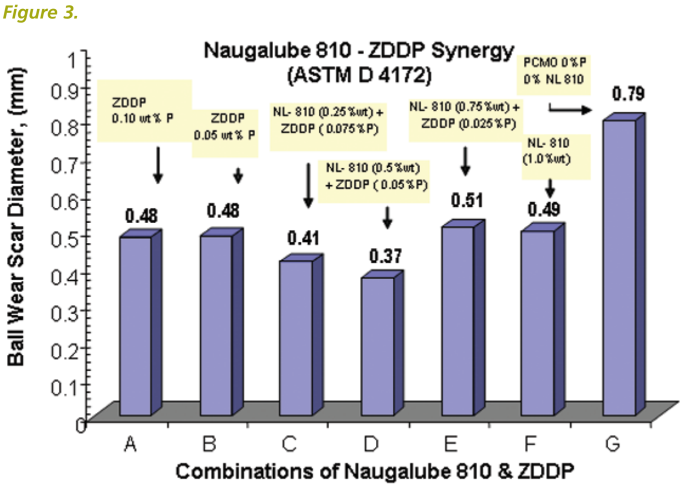
The principle need for developing OAW-FM additives free of phosphorus and sulphur is driven by a desire to reduce the demand on engine pollution control devises such as after treatment devices, exhaust catalytic converters, and particulate traps. These points are highlighted in Figure 2, showing the molecular structure of a typical ZDDP, and how it contributes to each factor. The R group represents a range of alkyl groups, linear or branched ranging from ~ 3 – 14 carbons.

Results and Discussion:

To develop and evaluate OAW-FM performance and compatibility with ZDDP, a number of tribology bench tests are first performed followed by real-world vehicle testing. Figures 3-6, presents the results of bench test data on a developed OAW-FM. Naugalube 810 was evaluated using Falex Four Ball (ASTM D 4172), and Cameron Plint TE77 Friction and Wear bench tests. The parameters for these bench tests are given in Tables 1- 3. Treat rates were kept constant to 1% wt total additive, (Naugalube 810 or ZDDP), with ZDDP expressed in terms of % wt. P, from the ZDDP. Since the ZDDP is 10% wt. phosphorus, 0.05% P is equivalent to 0.5% wt ZDDP. More specifically, a combination of 0.75% wt. Naugalube 810 and 0.025% P is equivalent to 0.75% wt. Naugalube 810 plus 0.25% wt. ZDDP. A Group II, 5W- 20 motor oil without phosphorus was used in the wear studies, and a Group II mineral oil used in the friction testing.

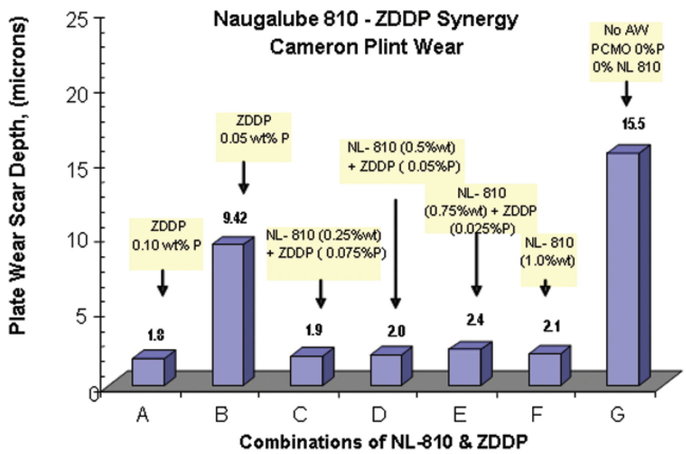
Figure 3.



Falex Four-ball wear results showing a synergistic combination of Naugalube 810 ashless organic antiwear-friction modifier additive and zinc dialkyldithiophosphate (ZDDP).

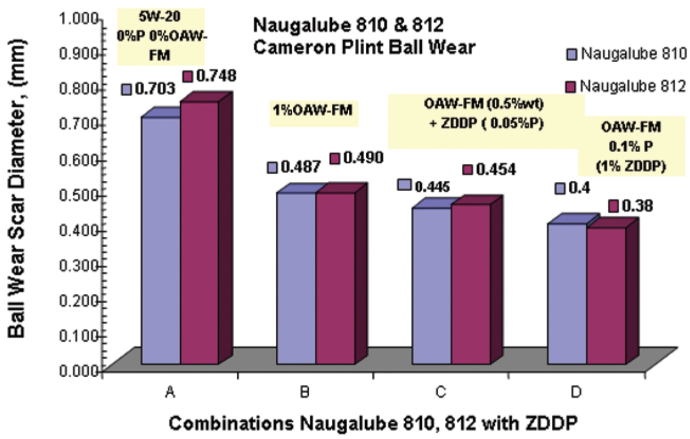
The results from Falex Four-Ball testing shown in Figure 3, indicate that the initial average wear scar diameter of 5W-20 oil (0.0%wt. P) could be reduced from 0.79 mm to 0.48 mm, with the addition of 1.0% wt. ZDDP (0.1% wt. P), or reduced to 0.48 mm using half this amount. This then is the Antiwear performance target. The OAW-FM (Naugalube 810 at 1.0% wt.) gives an average wear-scar diameter of 0.49 mm, and the combinations of 0.5% wt. Naugalube 810 and 0.5% wt. ZDDP (0.05%wt. P) showed synergy with the average wear scar diameter dropping below that of either additive to 0.37 mm.

Figure 4.



Cameron Plint Plate Wear Scar Depth (microns) showing improvement with the addition of Naugalube 810.

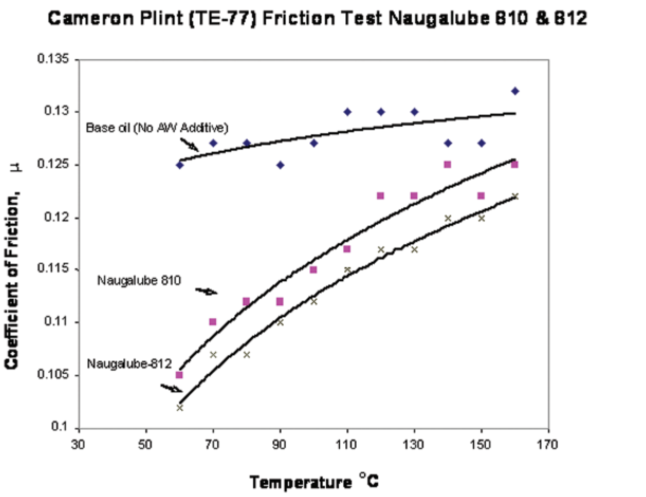
Figure 5.



Cameron Plint TE-77 Wear Tests run on two organic antiwear-Friction modifier additives Naugalube 810 and Naugalube 812, indicating the compatibility with ZDDP.

The Cameron Plint wear results illustrated in Figures 4 & 5, again show no loss of protection from the ZDDP even when reduced to 0.5%wt. ZDDP. In fact the plate wear scar depth is significantly decreased by adding 0.5% Naugalube 810 to 0.5% ZDDP (wear scar depth change of 9.4 microns to 2.0 microns). The blends of Naugalube 810 and Naugalube 812 with ZDDP at equal proportions, also shows equivalent performance in the ball wear scar width (Figure 5). This set of data like the previous, indicates the benefit of utilizing an OAW-FM such as Naugalube 810 or Naugalube 812 to reduce the concentration of ZDDP by half, without a loss of performance.

Figure 6.



Cameron Plint Friction testing of two ashless antiwear additives Naugalube 810 and 812 (at 1.0 % and 1.3% treat rate – to normalize for activity) indicating some friction modifier performance as well as antiwear performance.

In order to evaluate boundary layer friction modification with temperature, Cameron Plint Friction test data run on both Naugalube 810 and 812 is presented in Figure 6. The results show a measurable reduction in the coefficient of friction. Although there is a decrease in the reduction of friction with elevated temperature, Naugalube 812 shows a reduction in the friction coefficient ca. 12%, from 120 – 140 deg C.

Based on ILSAC objectives for GF-5 a number of recommendations were cited to address the need for an improved lubricant standard. These include fuel economy and fuel economy retention (Friction Modifiers), emission system additive compatibility (Antiwear to reduced sulfated ash particulate (% wt. P = 0.07% – 0.08%), increased high temperature engine oil (Antioxidants), longer drain intervals, compatibility to older engines, and use for turbo and supercharged and SIDI engines.

To meet these specific Antiwear/ Friction Modifier requirements, a performance level is needed to permit reduction in phosphorus to 0.05% w/o loss of AW protection, using as little sulphur or metals as possible. In addition, the technology needs to be non-corrosive to copper and lead, show seal compatibility, contain < 50 ppm Cl, be an oil soluble, low color environmentally acceptable liquid.

Naugalube 810 and Naugalube 812 meet these requirements and Chemtura data indicates compatibility with modern full formulated motor oils. Based on performance with ZDDP, it is expected that this class of organic additive does not compete for the surface with the ZDDP- glass film formation mechanism and in fact evidence shows a synergistic increase in overall antiwear performance has been observed.

1. Bovington, C., Friction, wear and the role of additives in their control, in Chemistry and Technology of Lubricants. Motier, R.M. and Orszulik, S.T. eds., Blackie Academic and Professional, London, pp. 329, 1997.

Table 1. ASTM D 4172 Four Ball Wear Test (Falex) test conditions

Four Ball Wear Test (Falex) ASTM D 4172 Test Conditions Samples Naugalube 810 & 812				
Load (N)	40 kG	Condition:	Temperature	75 C
			Rotation rate	1200 rpm
Selective catalyst : Cumene Hydroperoxide (1 wt%) JJ Habeeb, et al. SAE Paper 872157				

Table 2. Cameron Plint TE 77 Wear test conditions

TE 77 Wear Test (Cameron Plint) Test Conditions Samples Naugalube 810 & 812				
Load (N) Stage1	100	Condition:	Room Temp.-> 50 C in 15 min.	Hold for 15 min.
Stage 2	100		50 C -> 100 C in 15 min.	Hold for 45 min.
Stage 3	100	Specimen:	100C -> 150 C in 15 min.	Hold for 15 min.
Frequency	Hz= 30	1. Flat hardened Ground NSOH B01 Gauge Plate (RC 60/0.4_)		
Total Time:	1 hr. 15min	2. 6 mm Diam. AISI 52100 Steel Ball +/-20 kg/mm² hardness 3. Pro Wear Catalyst Cumene Hydroperoxide (1 wt %)		

Table 3. Cameron Plint TE77 Friction test conditions

TE 77 Friction Test (Cameron Plint) Test Conditions Samples Naugalube 810 & 812				
Load (N) Stage1	0	Condition:	Room Temp.-> 35 C in 10 min.	Hold for 5 min.
Stage 2	50		35 C -> 50 C in 10 min.	Hold for 5 min.
Stage 3	100	Specimen:	500C -> 160 C in 60 min.	End of Test
Frequency	Hz= 5	1. Flat hardened Ground NSOH B01 Gauge Plate (RC 60/0.4_)		
Total Time:	1 hr. 20min	2. Dowel Long Nitrided Steel Dowel Pin 6 mm (RC hardness 60)		

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Multisol Group to Distribute Lubricating Materials Based on ApNano Material's NanoLub® in Cooperation with InS R&D Company

ApNano Materials, Inc., a provider of nanotechnology-based products, has announced that the Multisol Group, a leading distributor of advanced lubricating materials in Europe, the Middle East and Africa, in cooperation with InS, an R&D company specialised in tribology, based in Genay, France, will begin to distribute in Europe high performance lubricant additives based on ApNano Materials' NanoLub® – the world's first commercial nanotechnology-based solid lubricant.

The innovative lubricants, containing NanoLub, significantly reduce the friction and wear of moving parts, and give excellent performance under extreme tribological conditions. NanoLub saves money, reduces pollution, is cost effective, safe and environmentally-friendly. Tests done under OECD international protocols prove that NanoLub is non-toxic or harmful. The enhanced lubricants are suitable for the automotive, industrial, aerospace and biomedical markets.

NanoLub is made up of particles of tungsten disulfide (WS2) that have a structure of nested spheres, called inorganic fullerenes. NanoLub lubricates using a combined mechanism: the particles lubricate by rolling like billions of miniature ball bearings and, in addition, the moving parts are covered with a lubricating thin film called tribofilm that covers the asperities or protrusions on surfaces, some only viewable under electron microscopes, that are the major cause of friction between sliding parts moving against one another. NanoLub is used as an additive to liquid oil or grease, and significantly enhances the lubricating properties of the oil or grease with respect to wear and friction by an order of magnitude. ApNano Materials produces NanoLub at its fully operational state-of-the-art automated plant in Israel.

Tests conducted both by leading academic institutes and by ApNano Materials' own customers have demonstrated NanoLub's superior lubricity features.

Multisol, a company with longstanding expertise in the European lubricant and additive market, has committed significant resources and capital to the market development of NanoLub over the next three years,. The agreement is the result of fruitful cooperation between ApNano Materials, Multisol and InS. Multisol recognizes the very important impact that nanotechnology and ApNano's materials holds for the future of lubrication and industry worldwide. Following the current agreement, the three companies will also continue their efforts in the field of special coatings based on NanoLub.

"The partnership between the three companies will enable European users to benefit from lubricants and greases that include a sophisticated and innovative nanotechnology-based additive with super-lubricity capabilities," said Dr. Menachem Genut, President and CEO of ApNano Materials. Dr. Genut was a research fellow in the original research group which discovered the inorganic fullerene nanoparticles at the Weizmann Institute of Science, Israel, and first to synthesise the new material. The group was led by Professor Reshef Tenne, currently the Director of Helen and Martin Kimmel Center for Nanoscale Science at the Weizmann Institute.

"ApNano Materials has already entered into the full commercial phase and we expect the demand for NanoLub to increase dramatically," said Aharon Feuerstein, Chairman of ApNano Materials. "NanoLub has attracted huge interest across the world."

InS will use its advanced tribological laboratories to identify the key areas for industrial application of NanoLub-based lubricants and to seek to maximise the benefits from the materials' unique properties.

"Since we have been working on extremely difficult cases of friction in various industrial sectors that we are covering, it is the first time that we find a material that answers such a wide range of friction issues," said Eric Gard, Managing Director of InS. "The more we study the material's properties and work on potential applications, the more we are convinced that Nanolub® represents a real revolution in lubrication. We have not seen that since the 1960s, when molybdenum disulphide additives were developed. NanoLub will bring a new era for the generation of lubricants."

Multisol, with its highly qualified application engineers, will promote these products in the lubricant manufacturing sector. "Multisol are delighted to be working exclusively with ApNano Materials, developing the market for this exciting new cutting edge technology," said Paul Oliphant, Multisol Group Chief Executive. "We are confident that we can help our European customers and suppliers discover excellent opportunities to significantly improve the performance of their products."

"We see very attractive perspective with this project, handled by Multisol France on behalf of the Group, and we can say that the first feedback received from the European lubricant market is already very promising."

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