ZDDP

Why, How, How Much?

Today's engine oils do a great job, thanks in part to the workhorse additive ZDDP. But what's in ZDDP? And why do some drivers and engine rebuilders insist they need more of this good thing? First of two parts.

Wear is as inevitable as the rising and the setting of the sun. It is universal in that everything that moves — or doesn't — wears. The ultimate expression of wear is entropy, that thermodynamic law which says that all matter and energy eventually runs down and becomes increasingly disorganized.

Given that wear occurs, the challenge is to delay it as long as possible. In an automotive engine that means retarding cam and lifter wear, ring and liner wear, rod and main bearing wear and so on. Most of the wear which occurs is in the ring and liner area since that is the largest surface in terms of square inches. However, the wear on cams and lifters often is more worrisome since the pressure between the surfaces is much greater.

Engine design can do much to reduce wear, but the most significant influence during operation is the engine lubricant. There are different facets to the antiwear properties of an engine lubricant and how they protect the engine.

The first factor is the oil's viscosity. Viscosity is the "thickness" of the oil and is the result of the internal friction between oil molecules. It is temperature related so as the oil becomes hotter the viscosity decreases. At some point, the oil becomes too thin to prevent metal-to-metal contact, and wear results. The oil property which most clearly reflects this is the high-temperature, high-shear viscosity of the oil. HTHS viscosity is measured under high-shear conditions at 150 degrees C and represents the absolute viscosity of the oil while discounting all additive effects.

That's a good start but there is much more that needs to be done to protect the engine. This burden is carried out by the additive package used in the engine oil composition. In addition to wear protection, additive packages contain a number of components which provide protection from sludge and varnish formation, oil foaming, as well as oil thickening.

Over the years, wear protection has

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been provided by a truly amazing component, a reactive chemical compound called metallic dithiophosphate. The metal used most commonly has been zinc, as in ZDDP or the variant ZDTP. Along with zinc, ZDDP brings both sulfur ("thio") and phosphorus into the oil in a form which lends itself to relatively low-temperature reaction with metal surfaces. This creates complex iron sulfide and iron phosphide layers on top of metal parts moving against each other within the engine. These chemical layers wear away with very little loss of surface area and without interrupting the operation of the engine.

Table 1. How Alcohol Selection Affects ZDTP

	Alcohol Type		
	Secondary Alkyl	Primary Alkyl	Aryl
Wear Protection	Excellent	Good	Average
Oxidation Resistance	Average	Good	Excellent

Within the chemical structure of the ZDDP molecule, the relative ratio of the key elements of sulfur/phosphorus/zinc is 2/1/1. Roughly speaking then, there is twice as much sulfur as there is zinc and phosphorus. (In actual calculations, there may be about 6 percent more zinc than phosphorus.)

Of this trio, the element attracting the most attention is phosphorus. Together with the sulfur, it is believed to bring the most antiwear functionality to the oil. For that reason, the level of phosphorus is watched most closely.

ZDDP comes in three distinct chemical structures, based on the type of alcohol used in the reaction process for making the finished product. Depending on the alcohol type selected, the finished ZDDP will have varying levels of wear protection and antioxidant performance (Table 1).

In earlier times, ZDDP was used at levels of up to 0.16 wt. percent in engine oils, and measured as zinc. This is because it originally was (and still is) viewed as a multipurpose additive in formulations, acting not only as an antiwear agent but also as a corrosion inhibitor and antioxidant. The earliest known applications in formulated engine oils date from 1941, when ZDDP was used as a corrosion inhibitor.

No one type of ZDDP can solve all problems though, so the choice of the proper material depends on what performance property is most important. For most passenger car and light-truck formulations, secondary alkyl ZDDP is the choice. It provides the best wear protection in spark-ignited gasoline fueled engines, where any shortfall in oxidation protection can be made up for with other types of antioxidants. It accomplishes all of this at levels of about 0.08 percent phosphorus.

By contrast, diesel engines rely on

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compression ignition, and their oil formulations usually employ a primary alkyl ZDDP with possibly some secondary alkyl mixed in. While loads are higher in diesel engines, the design is much more robust and doesn't need the high level of antiwear found only in secondary alkyl types. In addition, diesel engine oil formulations typically have a higher level of ZDDP, about 0.12 percent as phosphorus in the finished oil.

Engine expert Dick Kabel, formerly with General Motors Research, tells *Lubes'n'Greases* another element was at work in engines from the early 1920s until the mid-1970s: tetraethyl lead. Adding lead to gasoline boosted its octane and allowed engines to be built with higher compression ratios and hence better performance. But in order to prevent the buildup of lead and lead oxides in the engine, so-called lead scavengers were incorporated in the fuel. Usually these were ethylene chloride or ethylene bromide.

The drawback, Kabel reminded, was these reactive materials created highly acidic byproducts in the crankcase and tended to reduce the effectiveness of ZDDP. To counteract that, higher ZDDP dosages were used, often into the phosphorus range of 0.14 percent to 0.16 percent.

When lead was phased out from gasoline, he explained, it allowed some ZDDP reduction to take place. At the same time, engine metallurgy was improving to where parts could be manufactured with lower surface roughness. Both events led to more additive package optimization to get just the right alcohol type and level of ZDDP. Base stock refining improvements also allowed for more optimization, Kabel added.

The next logical step was to control ZDDP levels in engine oils. For one thing, automakers found that ZDDP decomposition products which got into the exhaust were being deposited onto cars' catalytic converters. One of these decomposition products, a compound called zinc pyrophosphate, formed a glass-like deposit on the catalyst, effectively blocking it from doing its job of converting exhaust gases into non-polluting materials. Phosphorus reduction in engine oil wasn't an immediate hit however, with many worrying that too little would lead to increased rates of wear.

Not all ZDDPs are alike, adds Don Smolenski, who is now the OEM liaison for Evonik Oil Additives after his own career with General Motors. In the 1980s, Smolenski managed taxi-fleet engine oil testing programs at GM. As GM and other automakers pressed for lower phosphorus and zinc levels, he recalls, formulators found progressively more effective ZDDPs to maintain the wear protection. He believes that the ASTM Sequence IV engine test, which measures scuffing and wear protection, gave pretty good insight into cam and lifter wear in particular.

Smolenski pointed out that the question of catalyst poisoning came to the fore in the late '80s, as today's ILSAC GF-series of engine oil specifications and the API Engine Oil Licensing and Certification System were being developed. From that point forward, phosphorus has remained a hot-button issue, with concerns raised both about higher levels and lower levels.

For some perspective, a look at the phosphorus limits in the API Service categories and ILSAC specifications makes it clear how the levels of phosphorus have been handled (Table 2).

Table 2. Putting a Lid on Phosphorus

	Engine Oil Designation		Phosphorus, wt%	
Year Introduced	Service Category	ILSAC Specification	min.	max.
Pre-1993	API SG and prior	—	—	—
1993	API SH	GF-1	—	—
1996	API SJ	GF-2	—	0.10
2001	API SL	GF-3	—	0.10
2004	API SM	GF-4	0.06	0.08
2010	API SN	GF-5	0.06	0.08
2017	API "SP"	GF-6	0.06	0.08

One of the fundamentals of the API engine oil system has been the concept of backwards compatibility. Simply stated, newer oil categories are required to be capable of servicing older engines — even engines designed around an earlier category. Given that the average age of cars and light trucks in the U.S. fleet at this time is pushing 11 years, it is almost certain that newer category oils are finding their way into older engines.

Looking at that aging fleet, it seems fair to say that the latest oils do a good job of controlling wear for the vast majority of vehicles on the road today.

However, there is a small and vocal body of end users who have another concern: those who build and drive high-performance vehicles or collectible cars. Their concerns center on the amount of wear protection needed for their engines, given that many of them are much older designs.

Lower phosphorus engine oils can be harmful to older engines, one enthusiast and rebuilder insisted to *Lubes'n'Greases*. "The worst-case scenario is engine break-in, as the cam and lifters polish each other, or tear each other up."

In fact, this source pointed out, the Engine Rebuilders Association recommends the use of diesel engine oil during engine break-in due to its higher ZDDP content. An advisory bulletin can be seen at www.aera.org/ep/techbulletins/TB2008/Q1-2008/TB2333R.pdf.

Other cautionary advice has come from the cam manufacturers Crane (www.aera.org/ep/techbulletins/TB2013/Q4-2013/TB2623.pdf) and Crower (www.crower.com/media/pdf/cam_book.pdf). Each warns that modern PCMOs are inadequate for engine break-in.

Is it possible for current, low-ZDDP engine oils to service these older vehicles and rebuilt engines, or is there a limit to what backward compatibility can do? More in part two, next month. ▮