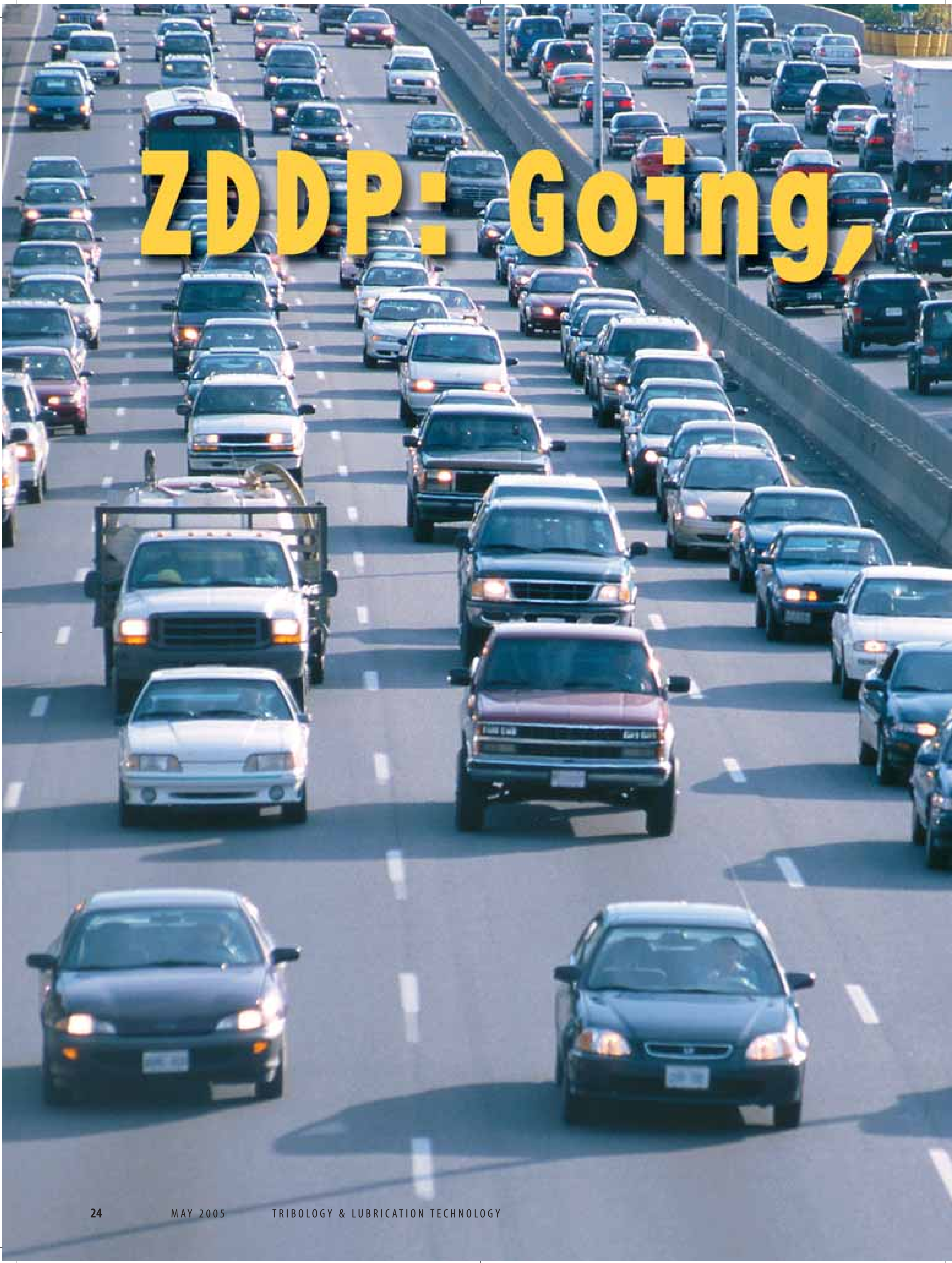
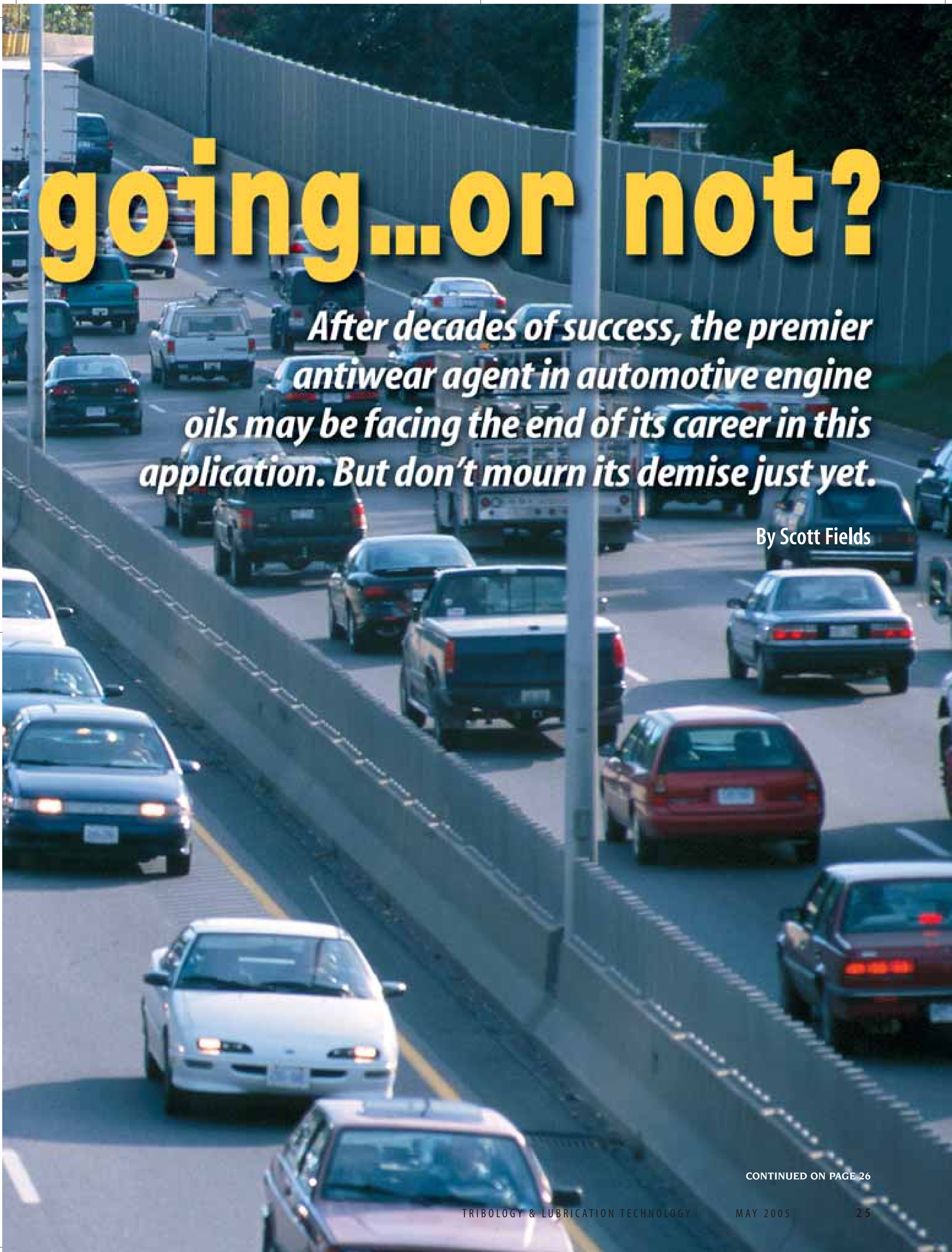


ZDDP: Going,



going...or not?

After decades of success, the premier antiwear agent in automotive engine oils may be facing the end of its career in this application. But don't mourn its demise just yet.

By Scott Fields

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Zinc dialkyldithiophosphates — ZDDPs — are a story of accidental success. Intended as antioxidants (they decompose hydroperoxides and peroxy radicals, which are the core of hydrocarbon chain reactions), their strength turned out to be as antiwear agents.

Now the very properties that led to ZDDPs' becoming perhaps the most successful family of lubricant additives ever may force them out of their biggest market, automotive engine oils. Currently about 30 million pounds of ZDDP is used in the United States alone. The vast majority of that ZDDP—almost 90 percent—ends up in engine oils for cars and light trucks.

In the 60 or so years since ZDDP compounds entered the marketplace, they have found their way into the vast majority of automotive engine lubricants as well as less widespread applications such as transmission and hydraulic fluids. (ZDDP's role in these applications is currently unthreatened.) And although ZDDP is used with a staggering variety of other additives, its basic function is constant, says STLE-member Hugh Spikes, professor in the Department of Mechanical Engineering at Imperial College in London, England. They tame oxidation and, more significant, reduce wear.

Until the end of the 1940s, ZDDP was relied on solely as an antioxidant; its anti-

(Photo courtesy of the Platinum Research Organization)

Dr. Harold Shaub (pictured left) of the Center for Innovation Inc. in Irving, Texas and Pranesh Aswath of the University of Texas at Arlington (UTA) confer at Aswath's lab, where Aswath and his colleagues are working on a catalyst that makes ZDDP more efficient, allowing it to appear in lower quantities in motor oil. The work is a collaborative effort between UTA, General Motors, and the Platinum Research Organization (PRO).

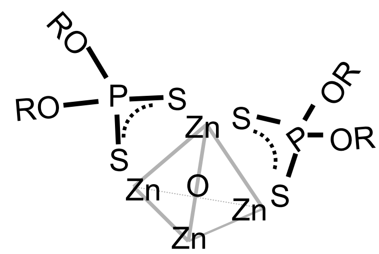
wear properties went unnoticed, Spikes says. And in the 50 years after, although engineers realized that ZDDP protected such vulnerable engine components as overhead valves, relatively little was known about the actual mechanism through which ZDDP reduces wear, he says. A flurry of research—prompted in large by pressure to find a substitute—has revealed more about how ZDDP works.

Three mechanisms through which ZDDP protects surfaces have been proposed, Spikes says. These possible mechanisms, he says, are (1.) formation of a mechanical film, (2.) stripping away of corrosive peroxides and (3.) absorption of abrasive iron oxide particles.

Most researchers, Spikes says, now believe that it's the first mechanism: ZDDP forms a protective film—a glass—on the surface of engine components. This zinc-phosphate glass, which is rich in zinc at the surface and then becomes higher in iron as it nears the metal's surface, becomes about 10 nanometers thick and somehow self-regulates to stay at that thickness.

"On rough surfaces, even when they're … not very hot, ZDDP actually forms a phosphate glass, a zinc-phosphate glass, a glassy solid, which is 10 to 20 or so nanometers thick and apparently just sits there and keeps the surfaces apart," Spikes says. "And if there's any wear, it's the film wearing off, and then it reforms on the metals. The actual mechanism by which that happens chemically, I'm afraid we still don't know."

Figure 1. Structure of basic ZDDP.



basic-ZnDTP, $(DTP)_6Zn_4O$
(two of four DDP ligands shown)

(Illustration courtesy of Dr. Hugh Spikes – Imperial College)

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ZDDP faces ousting from engine oils

This film—or glass—that ZDDP relies on to protect moving parts has led to pressure to reduce levels of the compound in automotive oil. The glass also damages another automotive component, the catalytic converter. In the engine, ZDDP volatizes, enters the exhaust stream and coats the converter's catalytic elements, which are usually platinum or palladium. This coating prevents exhaust from contacting the very catalyst that is meant to react with and control carbon monoxide gas and hydrocarbons.

"What seems to happen," Spikes says, "is that the additive is designed to form a phosphate glass on these metal surfaces, but some P_2O_5, or whatever it is, goes down the tailpipe and actually forms a phosphate glass on the catalyst."

The result is a shorter life for this expensive component, says Michael McMillan, manager of lubricant chemistry for Detroit-based General Motors. That's why, he says, automobile manufacturers have asked—or, really, required—oil producers to reduce the levels of ZDDP in their products.

Why, 30 years after catalytic converters became part of the American automotive landscape, do carmakers care now? Over the last two decades the U.S. Environmental Protection Agency (EPA) has steadily increased the amount of time that automobile manufacturers are required to warranty the catalytic converter, from the original 50,000 miles to 120,000 miles or 10 years starting in

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2004. Replacing a converter under warranty can cost hundreds of dollars, further shaving already thin profit margins.

Additionally, McMillan says, the EPA is gradually decreasing the amount of pollutants—including phosphorous and sulfur, which are found in ZDDP—cars and light trucks can release into the air. Reducing the amount of ZDDP in engine oil reduces the amount of phosphorous and sulfur at the business end of a car's tailpipe. Finally, ZDDP may reduce wear, but its phosphorous film increases friction between components and decreases fuel efficiency, Spikes says. Reducing ZDDP levels may actually increase gas mileage, a goal of carmakers hard pressed to meet corporate average fuel economy standards.

Automobile manufacturers clearly have a stake in the kind of oil that goes into their vehicles when they are delivered and throughout the life of the car, or at least its life during its warranty period.

Automobile manufacturers clearly have a stake in the kind of oil that goes into their vehicles when they are delivered and throughout the life of the car or at least its life during its warranty period. To protect their interests, representatives of the auto industry, including the Japan Automobile Manufacturers Association, DaimlerChrysler, Ford and General Motors, working as the International Lubricants Standardization and Approval Committee (ILSAC), set standards for engine oil.

GF-4, the most recent set of performance standards, calls for ZDDP levels of no greater than 0.08 ppm, a hard-fought compromise from the 0.05-ppm level some manufacturers had hoped for and a reduction of 20 percent from the 0.1 ppm of GF-3, says William Downey, vice president of the Petroleum and Energy Practice at Kline & Co., a New Jersey-based consulting firm. "For the lube suppliers and the additive suppliers, this is a significant change in the status quo," Downey says.

This standard virtually forces oil manufacturers to adjust their formulations with lower levels of ZDDP, Downey says. Although oil manufacturers are free to add as much or as little ZDDP, or any other legal additive, as they like, producing an uncertified product dooms it to niche markets.

"Manufacturers license their products through API, the American Petroleum Institute," McMillan explains. When these products meet the current GF specification, the manufacturers are "allowed to display a starburst certification mark on the front of the container indicating that they meet [ILSAC] requirements. Most manufacturers—General Motors certainly does, and I think most of the auto manufacturers do—indicate in their owner's manuals that people should use only products that display that symbol."

That puts oil manufacturers in the position of developing new formulas for each GF standard that are economical to produce and that protect well, Downey says. So far the reductions in ZDDP have been relatively modest, he says. But GF-5 is projected to drop ZDDP to 0.05 ppm and future categories could require ZDDP levels as low as 0.01 ppm or eliminate the additive entirely.

"The bottom line is that the oil additive companies are working towards 0.05%, but the automakers want it lower than that if they can get it," says STLE-member Dr. Harold Shaub, senior officer for knowledge and creative applications at the Center for Innovation Inc. in Irving, Texas. Shaub formerly was vice president of technology at Quaker State Corp. and a technical consultant for the Platinum Research Organization in Dallas. "The other half of the story is that the ZDDP chemistry has been run in the field for many years and, therefore, there's a lot of good, hard field data that says that it's very effective," he says.

ZDDP: Tough and tough to replace

Finding new chemistries, says Downey, could be expensive for additive companies, oil companies and consumers. "You've got this material that is relatively inexpensive on a dollar-per-pound basis and very cost-effective in the formulation because it acts both as an antioxidant and antiwear," Downey says. "To the extent that you pull that out, you have to replace with materials that are more expensive on a dollar-per-pound basis and are not multifunctional.

"If you pull the ZDDP, you have to add in both an antiwear and an antioxidant, and both at a higher price," Downey adds. "So there's been a concern in the industry that, as the OEMs, are saying, 'Just give me a lower chemical composition.' They're not focused on the performance and they're not focused on the cost."

Additionally, Shaub says, each new chemistry must meet the industry's "no-harm test," which cost about $150,000 and measures such performance parameters as wear, deposits and viscosity increases. "It takes us forever to OK an additive," adds STLE-member Paul Quinn, a process specialist for Quaker Chemical Corp. in Conshohocken, Pa.

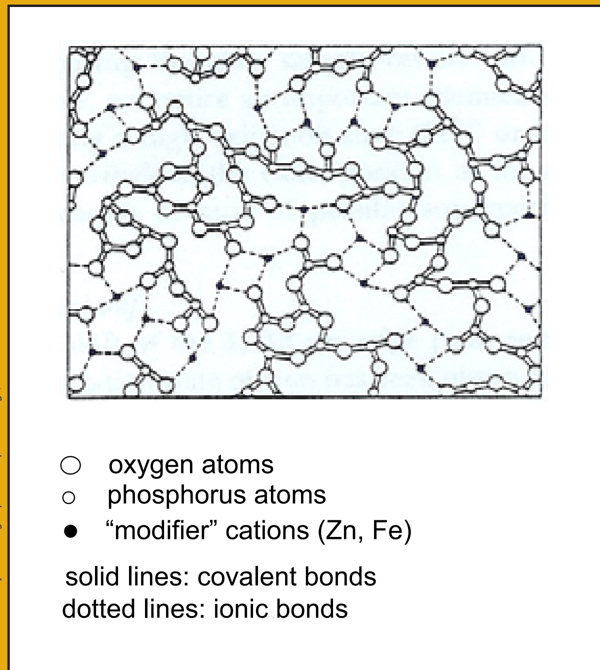
Even ignoring the expense of these tests and the time lag, replacing any mature technology can be a burden on the lubrication industry, Downey says. Fifty years of use have taught lubrication engineers a lot about formulation and formulability, stability, shelf life and other variables. The industry is also heavily invested in this dominant compound, he says. "They have plants that are making the stuff today. They've made an investment, and they're looking to defend that investment."

Currently, Spikes says, it's not clear that a good substitute for ZDDP exists at any price. "I've talked to a couple of [additive manufacturers] and some of them have said that they have this [replacement material]," McMillan says. "The thing is, if they do indeed have that kind of material, we've never seen it." That said, representatives for additive companies—such as STLE-member Betsy Butke, technology manager for industrial products at Lubrizol Corp. in Wickliffe, Ohio, which held the original ZDDP patents—say that they are prepared to adapt to any new market standard, although potential solutions are proprietary and thus far closely held.

ZDDP's impending diminished role—at least in automotive engine oils—has researchers scrambling for a substitute, says STLE-member Dr. Stephen Hsu, leader of the Nanotribology Group at the National Institute of Standards and Technology's Materials Science and Engineering Laboratory in Gaithersburg, Md. "Most people within the emissions community, including additive companies, are looking at various forms of boron chemistry," he says. "Boron chemistry also will give you a so-called solid glass structure." This technology dates back at least 26 years, he says, to patents by Chevron for metalworking fluids.

But boron and other candidates such as silicon have shortcomings when compared to ZDDP. Boron, for example, is susceptible to water hydrolysis. Another promising technology, Hsu says, is nanoparticles of metals suspended in lubricants. But this work, which originated in China, if not quite in its infancy, is far from ready for the

Figure 2. Schematic diagram of structure of a metallic glass.



(Illustration courtesy of Dr. Hugh Spikes – Imperial College)

'If you pull the ZDDP, you have to add in both an antiwear and an antioxidant, and both at a higher price.'

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market, he says. Or perhaps, says Spikes, high-molecular-weight ZDDP-like phosphorous compounds could prevent the materials from volatizing in the engine and coating the converter's catalyst. Such an approach, however, would require that phosphorous levels be set based on tailpipe emissions rather than the percentage of additives in oil.

lyst and ZDDP," he says, "and again we found that the reaction on the surface caused a surface modification, and the surface modification continued whether we had 800 ppm, 500 ppm or 100 ppm phosphorous in the ZDDP."

These phosphorous reductions, he says, not only spare the catalytic converter, reduce tailpipe phosphorous emissions and

EPA is gradually decreasing the amount of pollutants—including phosphorous and sulfur, which are found in ZDDP—cars and light trucks can release into the air.

Alternatives might allow ZDDP to stay

Rather than finding a substitute, another approach, says Pranesh Aswath, professor of materials science and engineering at the University of Texas at Arlington, is to find ways to make ZDDP more effective so that it can be used at very low levels. Aswath's group, working with the Platinum Research Organization (PRO) and General Motors, is testing a proprietary catalyst. "The bigger improvements that we're finding are enhancing the performance of ZDDP," Aswath says.

According to John "Corky" Jaeger, PRO's chief operation officer, this catalyst changes the way ZDDP interacts with metal surfaces. The catalyst, he says, when tested as an additive in the absence of ZDDP, chemically alters the surface of engine cylinders. But the catalyst on its own doesn't protect surfaces adequately.

"As we got further into the work and we started to look at engine oil and realized that nobody was going to eliminate ZDDP tomorrow, we decided that we'd better study whether the catalyst and ZDDP have a synergy," Jaeger explains. "The work then shifted to the interaction between the cata-

reduce friction, but the new chemistry is protective enough to allow lighter oil to be used as well. "Now, with the advent of a low-phosphorus engine oil and a five-weight (5W) oil, there could be a huge environmental impact," he says.

Meeting proposed ZDDP levels of 0.05 ppm—and perhaps as low as 0.01 ppm—for GF-5, which looms in 2008, is a tall order, says Downey. But, says Spikes, eliminating ZDDP altogether is much trickier. The very properties that make ZDDP so effective could make a substitute just as problematic.

"It's not just a matter of finding something that works," Spikes says. "It's also a matter of finding something else that works and that doesn't harm the catalyst anyway. Things that form films on surfaces, if they get down the tailpipe, are quite likely to form protective surfaces on catalysts." **<<**

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