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ADDITIVE TREN

Zapping SAPS, Cutting Costs & Tackling Toxins

TLT's poll of top additive-company managers provides an insider's look at the trends that will be driving emerging technologies in the next five years.

By Kathryn Carnes
Features Editor

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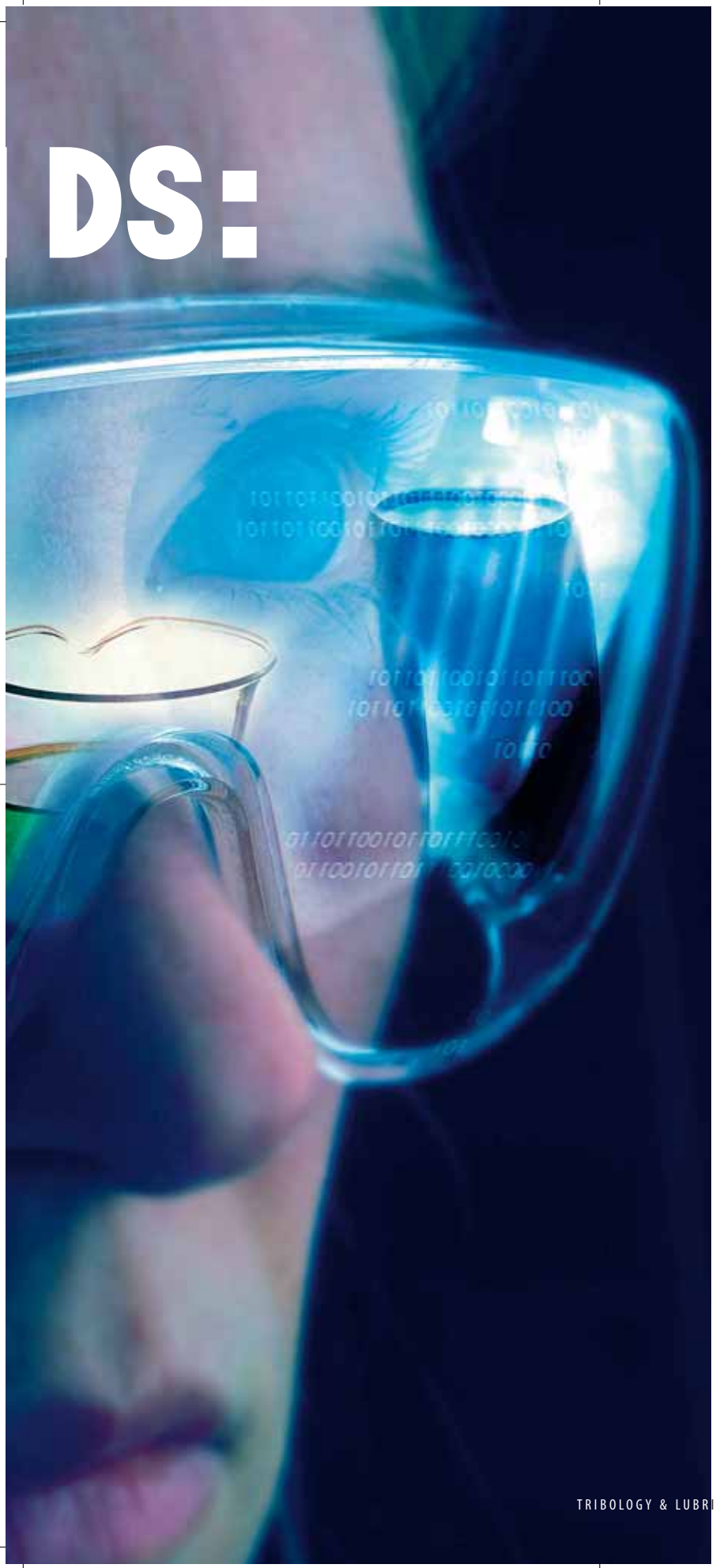

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In June TLT conducted an informal survey of executives with the industry's leading lubricant additive companies to gain insight into their current activities and vexations. We also hoped to get some notion of how they expect to be affected by certain high-profile and extensive regulatory initiatives—particularly in the United States but in Europe as well.

In short, we wanted to hear straight from the horse's mouth how additive technologies will continue to evolve in the next five years. We also were interested in hearing about the key drivers of that change.

For our informal poll, TLT e-mailed a survey instrument to 233 execs and garnered 39 usable returns for an 18% response rate. The types of additives and additive packages our respondents manufacture and market are shown in Figures 1 and 2 (*see page* 35). Unaccountably, the survey developer (who also happens to be your humble scribe) failed to include antioxidants among the choices of additive types. Assuming that antioxidants are manufactured about as often as antiwear or extreme-pressure agents, the percentage of manufacturers offering antioxidants has been estimated conservatively at 50% in Figure 1.

Very few of the respondents market automotive engine oil packages, with only 9% offering passenger car motor oil (PCMO) or heavy-duty diesel engine oil (HDEO). Instead, a high percentage of the respondents are focused on industrial applications. Only 32 of the 39 respondents reported marketing additive packages, with metalworking fluid packages proving most popular at 50%.

Now let's take a look at what you're waiting for—emerging trends in additive technology.

Trend 1: Zapping SAPS in HDEO

The first market question we asked our execs was, "During the next five years, in which area do you expect most of your additive product R&D expenditures to be focused?"

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(Photos courtesy of Lubrizol Corp.)

Additive companies are currently hard at work on finding ways to meet U.S. PC-10 heavy-duty diesel engine oil specifications. The emissions requirements are driving the development of new low-/no-sulfated ash/phosphorus/sulfur (SAPS) oils—the top trend in our survey.

Despite the breadth of industrial and metalworking offerings among our survey respondents, automotive applications got the nod as being the area in which most R&D expenditures would be focused during the next five years.

Despite the breadth of industrial and metalworking offerings among our survey respondents, automotive applications got the nod as being the area in which most R&D expenditures would be focused, with 56% of respondents selecting this option. This level of attention is understandable given the pace of engine oil specification changes and the pressure that has been put on specific additive chemistries. Phosphorus, for example, is under fire on both the PCMO and HDEO sides, and sulfur (on its own and as a component of ash) is being pushed out of diesel fuel and HDEO because of its negative effects on emissions.

Additive companies are currently hard at work on finding ways to meet U.S. PC-10 specifications issued by the Engine Manufacturers Association; accordingly, the need for low-sulfated ash/phosphorus/sulfur (SAPS) HDEO was highlighted frequently in our survey. TLT took a closer look at PCMO, especially the drive to remove phosphorus in the form of zinc dithiodiphosphate (ZDDP), in our May 2005 issue (*see page* 24).

PC-10, which will define the next American Petroleum Institute (API) licensing category for HDEO, was necessitated by the U.S. Tier III emissions legislation that will be implemented between 2007 and 2010. The new rules call for particulate matter (PM) emissions to drop to 0.014 g/kW-h effective in 2007 and nitrogen oxide (NOx) emissions to be capped at 0.27 g/kW-h by 2010. As part of this effort, the EPA has reduced allowable diesel fuel sulfur limits to 15 ppm by mid-2006.

To meet the emissions standards, engine makers are turning to aftertreatment devices that supplement exhaust-gas recirculation. In the United States, engines are being equipped with diesel particulate filters, while in Europe selective catalytic reduction is favored.

These aftertreatment systems are, however, susceptible to fouling by SAPS components, which are typically used in the detergents, antioxidants and antiwear additives that have enabled heavy-duty engines to meet their long lifetimes (now averaging about one million miles of service). Thus, the PC-10 specifications are forcing lube formulators and additive companies to accept chemical limits of these components, with sulfated ash limited to 1.00 mass% maximum by ASTM D874, phosphorus to 0.12 mass% maximum by ASTM D4951 and sulfur to 0.4 mass% maximum by ASTM D4951 or D2622.

The problem with losing the SAPS components is that they have "proven to be extremely effective for retaining engine oil base number, controlling oxidation and limiting deposit formation," says STLE-member Vincent Gatto, senior advisor-antioxidant applications, CTS & product development for Albemarle Corp.'s Baton Rouge, La., office. "A real dilemma exists regarding oxidation: While current sulfur and phosphorus chemistry is detrimental to catalyst and engine aftertreatment systems, it's really the only adequate low-cost option for decomposing peroxides during comprehensive oxidation control. Peroxide decomposition is one of the critical steps for inhibiting oxidation of the lubricant.

"So SAP components are not going away very soon," Gatto adds. "What I believe we will see over the next several years is new metallic, sulfur and phosphorus chemistries that are significantly better performing then current chemistries. Also, greater use of molybdenum and improved molybdenum compounds as multifunctional antioxidant/antiwear additives. This will allow reductions in these elements without impacting wear, oxidation and deposit control."

In addition, Gatto says, traditional antioxidant chemistries—such as hindered phenolics (which Albemarle manufactures) and alkylated diphenylamines—will be incorporated at higher levels.

"However, in many formulations there will be an upper limit regarding the use of these materials," he cautions. "To address this, optimized antioxidant systems and new antioxidant chemistries will have to be developed. These new chemistries, in fact, may require some multifunctional properties."

On top of emissions concerns is the not-unrelated goal of improving fuel economy, a

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topic on the minds of several survey respondents. Although engine technology itself has improved in this regard, such gains have been facilitated and extended by the development of engine oils with lower and more stable viscosity. Charles Dustman of RohMax Additives USA's Horsham, Pa., office, notes that the viscosity index improvers his company makes can help formulators meet both efficiency and emissions goals. "As you improve efficiency, you are able to do a unit of work while consuming less fuel, which decreases emissions. From our perspective, carefully formulated high-viscosity index fluids using appropriate shear-stable viscosity index improvers can improve efficiency and emissions at the same time, which, we think, is of significant value to the industry."

Related to PC-10, the TLT survey elicited several optimistic responses to the open-ended question: "What 'intractable' lubrication problem do you think will be overcome by additive technology in the next 5 or 10 years?" Perhaps because there is a sense of urgency to do so, the development of low-/no-SAPS engine oils topped the list. Replacement of ZDDP was singled out for particular attention, although sulfur reduction and ashless chemistry also were mentioned.

"The potential reductions in the levels of sulfur, phosphorous, and ash—ZDDP—is one of the biggest changes I have seen in the lubricants business," says STLE-member Bruce Calvert of Uniqema, headquartered in New Castle, Del. "I think we can solve that with additive chemistry, which will be a milestone for this industry."

While there may be a sort of universal call for low-/no-SAPS HDEO, some respondents hinted that heavy-duty engine technologies will begin to vary enough between companies and between regional/national markets to render industry-wide specifications relatively insignificant.

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Figure 1. Additives Manufactured by Survey Respondents

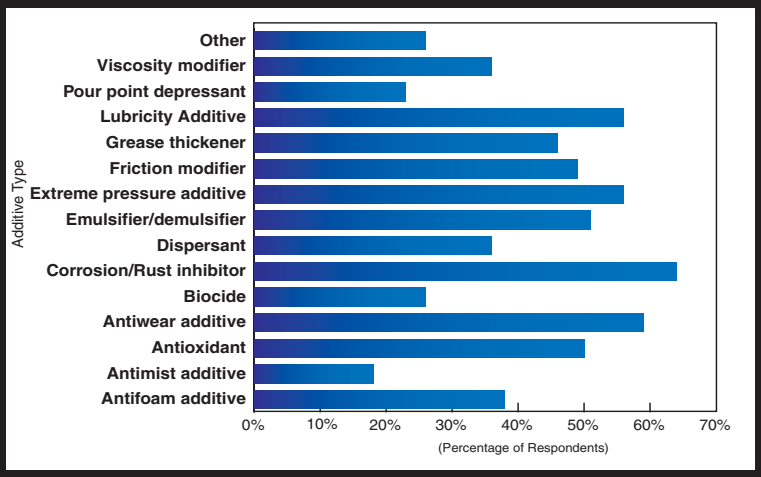


Figure 2. Additive Packages Marketed by Survey Respondents

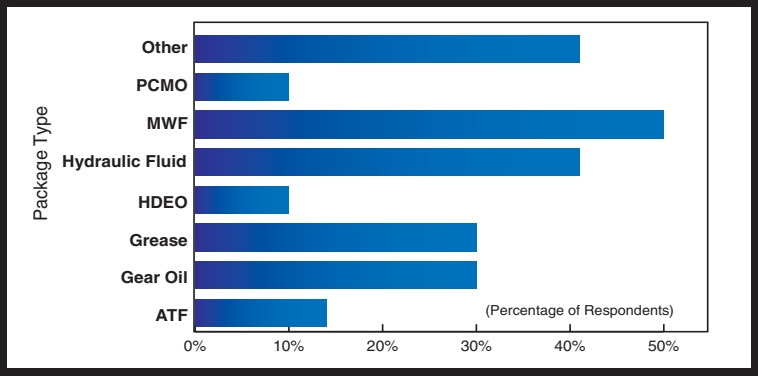


Figure 3. Extent to Which Advanced Formulation and Test Techniques will Offset Organization's Financial Pressures

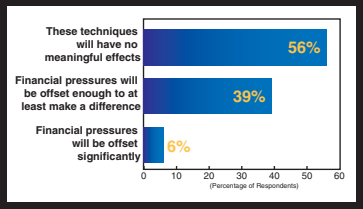


Figure 4. Extent to Which Advanced Formulation and Test Techniques are Improving Additive R&D

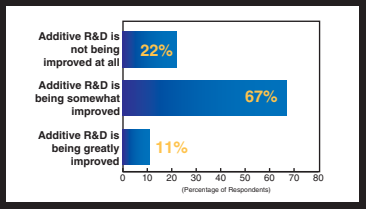
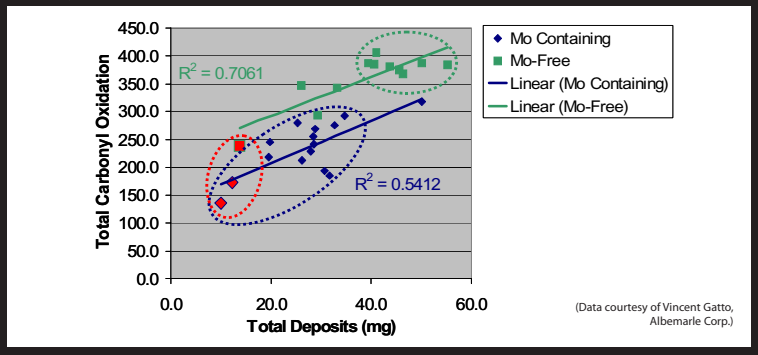


Figure 5. Total Carbonyl Oxidation = [Volatiles Carbonyl Peak Area * wt] + [Rec. Oil Carbonyl Peak Area *wt]



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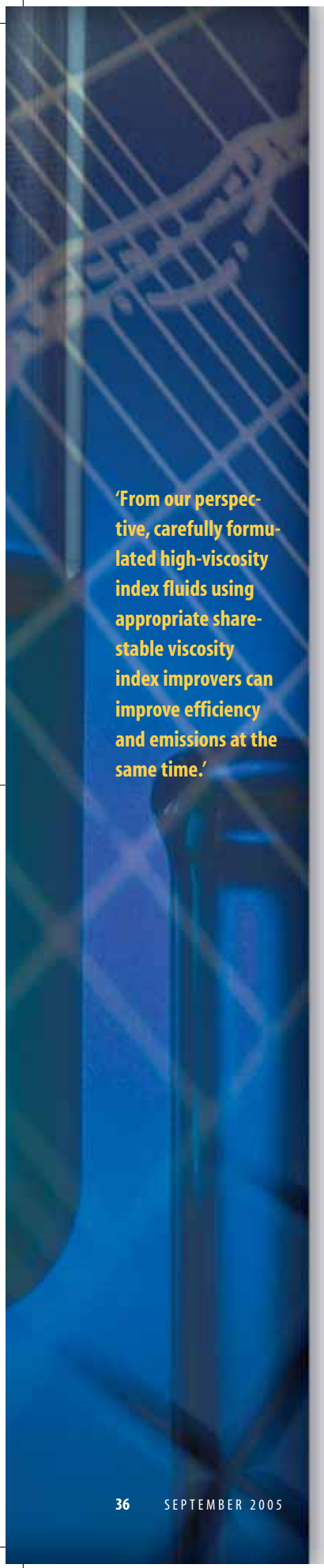

'From our perspective, carefully formulated high-viscosity index fluids using appropriate shear-stable viscosity index improvers can improve efficiency and emissions at the same time.'

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Some would argue that this is already the case: HDEO marketers typically qualify their products to both the API's industry-wide licensing standards and stricter individual-OEM (Mack, Caterpillar, Cummins, etc.) specifications.

"From a technology viewpoint and in an effort to control heavy-duty diesel development costs, it eventually may make sense to have OEM-specific lubricant specifications as opposed to industry-wide specifications," said John McChesney, global business manager-antioxidants for Albemarle. "Diesel engine technologies may diverge to a greater extent as sulfur levels are driven lower and as quantum leaps in fuel economy are sought. The oil industry and the downstream service sector are fairly well positioned to handle 'OEM oils' in the [heavy-duty diesel] market. On the passenger car side, engine technologies remain fundamentally similar; therefore, industry specifications most likely will remain for a long time."

In addition, McChesney noted, passenger car oil changes are handled in a more diverse marketplace. "It is one thing for the car dealership to carry the branded oil but a far more difficult task for the independent oil change operator to carry numerous engine oils for each OEM," he said.

Differences in engine oil additive development that do arise for passenger cars will likely be due to regional differences that have promoted different fuels, said Vince Livoti of Ciba Specialty Chemicals, headquartered in Basel, Switzerland, with U.S. headquarters in Tarrytown, N.Y. "Europe and the U.S. are headed down different paths over the next five years. Europe's passenger car fleet comprises a much larger percentage (~40%) of diesel vehicles due to tax advantages consumers realize by owning these cars.

"Thus, European oil specifications are largely driven by reduction of sulfated ash. Conversely, since the U.S. passenger car fleet is predominantly gasoline powered (97%), U.S. engine oil standards are driven by reduction of phosphorus. Different additives and formulation techniques will be needed to help both sides of the Atlantic meet the needs of their respective fleets."

Despite this seeming flood of change, lube formulators and additive companies have long complained that engine oil specification changes are (in a sense) implemented too slowly. That is, stepwise implementation of standards and the resulting incremental changes in engine technologies create unnecessarily burdensome work for the additive manufacturers and lube marketers by necessitating continual stepwise reformulation of engine oils, with an associated high cost of additive R&D and testing during engine oil development and certification.

These costs have long nettled additive companies, which have little time to recoup their investments before the next set of incremental specs is issued. This, too, was reflected in our survey. Several respondents said their companies would prefer that automakers change specifications less often but that the changes called for in new specs be more substantive.

Not that anyone expects this, however. "We believe that changes in passenger car gasoline engines will be incremental," said Mayur Shah, global technology manager for Lubrizol Corp., headquartered in Wickliffe, Ohio. "The changes in heavy-duty diesel engines also will be incremental. We understand the regulatory demands that force the OEMs to modify engine designs, which, in turn, drive the need for changes in lubricant requirements.

"Chemical restrictions (driven by the need to protect aftertreatment devices), coupled with increased lubricant performance requirements, have had an impact on lubricant technology, which plays an increasingly significant role in delivering performance and environmental value," Shah adds. "However, recovering return on investments is becoming increasingly difficult, and as an industry we have not been able to extract the true value in the marketplace."

Trend 2: Cutting costs through bench testing

If costs cannot be recouped by changing engine oils less frequently, then perhaps the nature of R&D or of testing itself should be changed, said several survey respondents. As for R&D cost reduction through such techniques as computer simulation, molecular engineering and similar approaches to formulation planning and testing, additive companies expressed hopeful caution. Most respondents indicated that additive R&D is being somewhat improved by these techniques, but more than 20% said they are not

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Figure 6. Ratings of Factors in Additive Development for the Next 5 Years

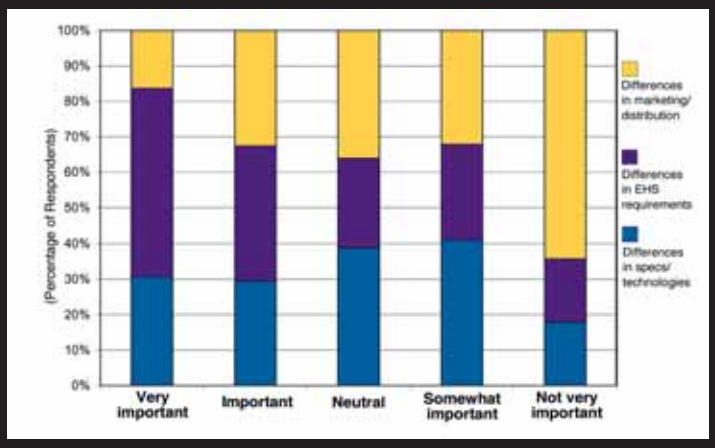
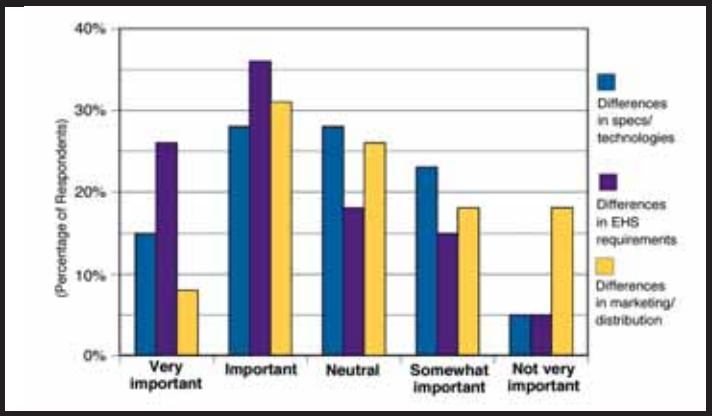


Figure 7. Importance of National/Regional Factors in Additive R&D for the Next 5 Years



Engine tests are thorough but time-consuming and expensive. Additive manufacturers we surveyed said they would like to replace some engine testing requirements with bench tests, which take less time and cost less.

helping at all (*see Figure 3 on page 35*). Very few of the respondents reported incorporating any of these types of tools in their own labs, and among those who did, 20% said the results were only so-so or even disappointing (*see Figure 4 on page 35*).

More often, respondents mentioned substituting appropriate bench tests for some engine/rig tests in HDEO and PCMO certification testing. There is precedent, some noted, specifically calling attention to the Ball Rust Test (ASTM D6557), an 18-hour bench test that in 2003 replaced the Sequence IID test (ASTM D5844) beginning with ILSAC GF-3/API SL to evaluate a lubricant's ability to prevent engine corrosion, particularly rust formation.

"In the early stages of the Ball Rust Test development, one of the key criteria for test acceptance involved properly ranking industry reference oils relative to the IID test," said Albemarle's Gatto. "This was a difficult task initially because additive chemistries in the reference fluids showed differing responses between the two tests. Our approach [at Ethyl Corp., which spun Albemarle off in 1994] was to gain an understanding of component response in the test. The use of designed experiments with model formulations helped pinpoint specific chemistry types that were both beneficial and detrimental in the test. Having this knowledge, we were able to redesign the test to more properly rank the reference oils."

A similar scenario may be playing out for the Thermo-Oxidation Engine Oil Simulation Test (TEOST), which, Gatto points out, is part of the current GF-4 PCMO specifications.

"We believe this is a very useful test for research in that both deposit tendencies and oxidation characteristics of an engine oil can be studied," Gatto said, offering some data presented at this spring's STLE Annual Meeting in Las Vegas (*see Figure 5 on page 35*). "Correlation of TEOST results to field performance is still an area that requires more work, but its importance as a deposit test bench tool for research cannot be stressed enough."

In this case, of course, the TEOST would not replace engine testing but would be used to screen candidates for formulation

(in theory, at least, thereby reducing the number of formulations that would be submitted to engine testing without hope of passing). For a more complete picture of various aspects of oxidation, Gatto suggests, a spectrum of tests might be used. At Albemarle pressurized differential scanning calorimetry, the Caterpillar Micro-Oxidation Test and Albemarle's Bulk Oil Oxidation Test are used to supplement the TEOST.

"This approach provides a fundamental understanding of oxidation processes under a variety of environments," Gatto said. "Any new antioxidant or antioxidant system that performs well in all these tests is likely to perform well in most engine tests and in the field…to be 'robust.' A robust formulation should make a good starting point for formulations that could then be subjected to a more limited set of potentially lower cost engine tests."

The cost of engine/rig tests is a primary but not sole concern with their use. "Add in the variation in the tests, the difficulties in developing acceptable tests in a timely fashion and operational issues (engine and parts availability, access to qualified test stands, etc.) and it is easy to see why it is that, despite the excellent and diligent work of those developing the test methods, there is a continuing need for simpler bench test equivalents," RohMax's Dustman says. Lubrizol's Shah added that his company sees a need for expanded base oil interchangeability and viscosity read-across guidelines from the API, which would allow for base oil substitutions without necessitating complete qualification retesting for engine oils.

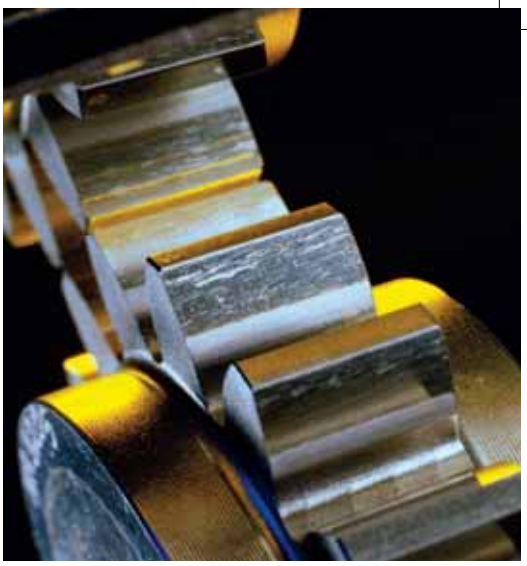
But perhaps the most welcome change of all, said Uniqema's Calvert, would be a little less attention from regulators. "We are hopeful that perhaps once these initiatives are in place around sulfur reduction, phosphorus reduction and ash reduction…that the pace of legislative change will slow down a bit," he said. "We have just been through a period of extraordinary change driven by important measures to protect the environment. This has placed a tremendous burden on the auto and oil industries."

Trend 3: Tackling toxins, industriously

Automotive applications are not the sole focus of environmental legislation. Industrial oils are also under scrutiny for their environmental effects and eco-toxicity. In addition, these fluids are subject to increasing regulatory pressure to improve their worker safety and health profiles. Thus, also ranking high in our responses (enough to constitute our third identified trend among respondents) were pressures stemming largely from environment, health and safety (EHS) concerns related to industrial fluids.

Some of the concerns are rather across-the-board; others tend to vary by region/nation, our survey respondents indicated. Figures 6 and 7 show that national and regional differences in EHS regulations and legislation during the next five years were judged to be "very important" or "important" drivers of distinct additive products by 63% of survey respondents. Conversely, only 43% said regional/national differences in industry specifications or technology status during the next five years were "very important" or "important." National/regional differences in marketing and distribution were judged to be relatively unimportant, with only 8% of respondents calling them "very important" drivers of additive development.

Specifically mentioned were the long-standing expectation that large users and governments will call for chlorine to be removed from metalworking fluids, cleaners and the like and anticipated reductions or elimination of heavy metals such as lead, cadmium, molybdenum and mercury. Also mentioned by various respondents were such concerns as biocides/bacteria, amines/pH/corrosion inhibition and overall levels of additives in formulations/multifunctional additives.



Industrial oils are under scrutiny for their environmental effects and eco-toxicity. In addition, these fluids are subject to increasing regulatory pressure to improve their worker safety and health profiles.

Many of these concerns become intertwined as additives are developed. For instance, "Our metalworking fluid formulator customers have been asking for additives that render the metalworking fluid emulsion less susceptible to bacteria and fungus growth," says STLE-member Brent Brennan, marketing manager for Degussa Goldschmidt Chemical Corp., headquartered in Basel, Switzerland.

"As regulations and end-user perceptions of biocides tighten, formulators are seeking alternatives that minimize the health/exposure risks associated with metalworking fluids, Brennan adds. "Like many suppliers, we do not market biocides, and we do not claim our products are effective at eliminating bacteria from a metalworking fluid sump. However, as a full-line supplier of performance additives to the metalworking fluid market, we are seeking ways to develop products that extend the life of the fluids in which they are formulated."

One such chemical, dicyclohexylamine (DCHA), has received some attention in the literature for its biocidal properties. However, cautions consultant Wheeler Crawford of Canyon Creek Chemical Consulting

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Several respondents said their companies would prefer that automakers change specifications less often but that the changes called for in new specs be more substantive.

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in Houston, amine chemistries (especially secondary amines, which form carcinogenic N-nitrosamines) are under fire for their EHS profiles. One, diethanolamine (DEA) has been banned from metalworking fluids in some European countries and "is considered anathema here [in the U.S.], too," Crawford notes. "There are problems in Japan, U.S., and Europe with MEA (monoethanolamine)-containing fluids, which are banned at some automotive plants."

Amines are looked to principally for pH, pH control (buffering) and inhibition of ferrous metal corrosion, Crawford notes, adding that several substitute chemistries exist, although there might be some cost penalty for using them. Still, such substitutions may be required.

"Amines, collectively, are on some hit lists because of their high pKa, volatility and irritation potential," Crawford said. "The amine issue can be emotional, but one must be careful not to throw the baby out with the bathwater. There are certain selection criteria that should be used in selecting an amine for a metalworking application. The first must be its environmental, health and safety profile, including such things as a proper balance between biostability and biodegradability, volatility, pKa, skin irritation, odor and metal-leaching characteristics. The second criterion is performance." In some cases, Crawford notes, reducing the level of a particular amine might necessitate increased use of biocide, corrosion inhibitor or pH buffering agents, even if the overall drive is to reduce additive treat rates in formulations.

The importance of EHS issues to additive makers' businesses was reflected in our survey respondents' answers to questions about how they expect the industry to be affected by various governmental programs on chemical toxicology and safety. Asked "How do you think legal liability issues related to REACH (Registration, Evaluation and Authorization of Chemicals), HPV (High Production Volume), Endocrine-Disrupter and similar programs will affect the number of additive companies during the next five years?" 70% of respondents said they expect that there will be fewer chemical manufacturers serving the lubricants industry. Ditto for how they think these programs will impact formulations: 83% said formulators will have fewer additive choices due to the elimination of chemical options.

Conclusions

SAPS in engine oils, cost controls and EHS issues loom large in additive makers' minds at the moment. Nevertheless, the industry seems confident that none of these challenges is insurmountable. Perhaps because these additive manufacturers recently survived a very busy era of corporate restructuring and consolidation—with many of them bulking up in the process—they feel strong enough to tackle these tough issues. They also apparently expect that new, safer, better-functioning additive choices will result from these efforts—setting a trend that should prevail for many years to come. **<<**

You can contact Houston-based writer Kat Carnes at **k.carnes@sbcglobal.net**.

Solving lubrication's 'intractable' problems

TLT asked our surveyed additive executives, "Which 'intractable' lubrication problems do you think will be overcome by additive technology in the next five years? 10 year?"

- Multifunctionality—creating multipurpose oils and lubricants.
- The development of high-performance ashless formulations.
- Nothing in the next five years. In the next 10 years we'll have SAP-free additives.
- We will replace zinc dithiophosphate and come up with improved antioxidants to take products to greater temperatures.
- Robust, low-phosphorous and low-SAP engine oils.
- Cost pressures and declining markets will significantly reduce the amount and impact of industrial additive development. The only significant development will be in mandated areas.
- Longer change levels for all lubricants.
- Corrosion reduction.
- Better emission system compatibility.
- Solving the incompatibility of antiwear systems with catalytic converter systems. **<<**