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## Special Report: Trends in extreme pressure additives

**F**ormulation of industrial lubricants requires the selection of a number of different additive types such as antioxidants, corrosion inhibitors, defoamers, emulsifiers, extreme pressure (EP) agents, lubricity additives, pour point depressants and viscosity index (VI) improvers. Within each category, the formulator is also faced with having to select specific chemistries for use in preparation of the lubricant.

This leads to concern from a formulation standpoint about whether the additive will not only provide the required performance but also how it will impact the other components in the formulation.

This is a major issue that lubricant compound/blenders must deal with on a daily basis.

TLT conducted a readership survey in mid-2007 and asked readers which additive type has the greatest impact on the performance of their lubricants and which additive class they would be most interested in learning more about. Overwhelmingly, reader response was that EP additives have the greatest impact on lubricant

performance. The survey indicated that readers wanted to learn more about this additive type in order to better understand how to use them in formulations.

TLT sought interviews with the industry's key additive manufacturers to gain insight on this additive class. The five EP suppliers who agreed to talk are, in alphabetical order, Arkema, Dover Chemical, Lubrizol, Rhein Chemie and Rhodia.

An initial discussion was held to provide basic information on how EP additives function and the various technologies available to the formulator.

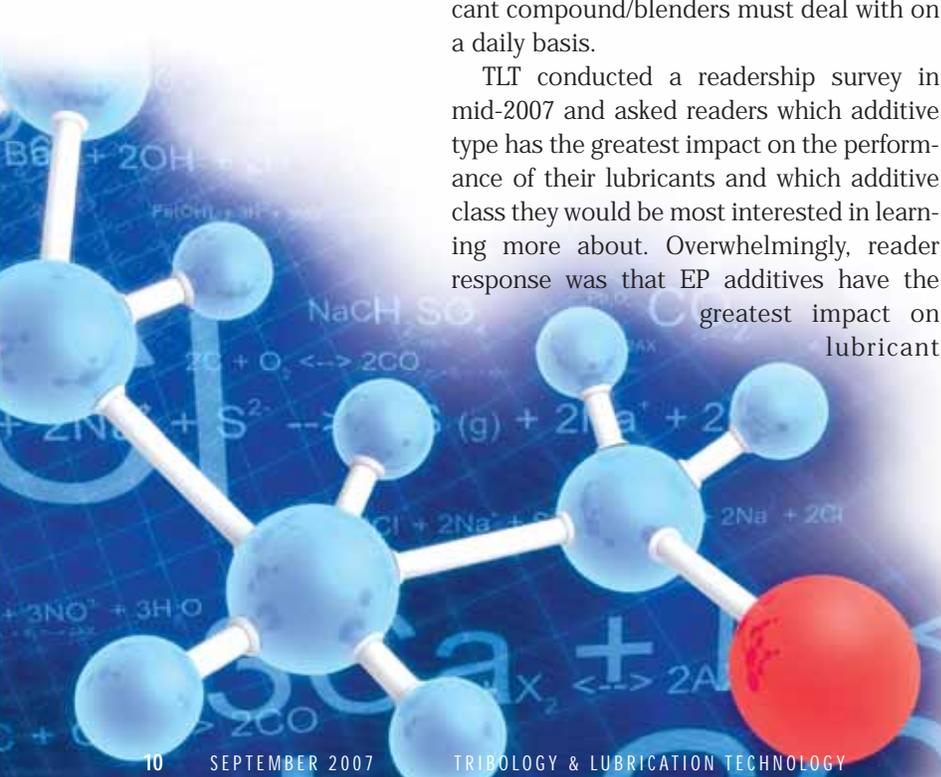
### What is an EP additive?

Lubricants operate in the boundary between moving metal parts to prevent the contact that could lead to an increase in friction, increase in wear and eventually welding. The classic type of component used to prevent these phenomena is a boundary lubricity additive.

The boundary lubricity additive typically functions by adsorbing on the metal surface to form a film that will reduce metal-to-metal contact. This function is achieved because the boundary lubricity additive has a polar head group that can interact with the metal surface and a tail group that is compatible with the lubricant carrier (mineral oil, synthetic basestock or water). A classic example of a boundary lubricity additive is an ester which could be available as a natural product (canola oil, lard oil, tall oil fatty acid, etc.) or as a functionalized molecule (monobasic ester, diester, polyol ester, complex ester).

As the conditions under which metal-to-metal interactions become more severe due to higher temperatures and pressures, the lubricant becomes more stressed. The dis-

Traditional boundary lubrication additives do not remain on the metal surface and cannot prevent the increasing friction, wear and damage to the machinery seen under these conditions.



tance between the metal surfaces has decreased to the point where rubbing is occurring and welding becomes more than just a remote possibility.

Traditional boundary lubrication additives do not remain on the metal surface and cannot prevent the increasing friction, wear and damage to the machinery seen under these conditions. Extreme pressure additives are required in order to enable the specific application operating under these conditions to continue.

There are four main types of extreme pressure additives that are based on chlorinated, phosphorus, sulfur and overbased sulfonate species. The first three EP additive types are activated by reacting with the metal surface within a specific temperature range. In comparison with boundary lubricity additives that operate from ambient temperature up to 200 C, chlorinated additives are activated at a temperature between 180 C and 420 C. Phosphorus operates to a higher temperature and sulfur at an even higher range that ends at 1,000 C.

Figure 1 shows the operating range for these three extreme pressure additive types. In reacting with the metal surface, these three additive types form iron chlorides, iron phosphides and iron sulfides, respectively. The metal salts produce a chemical film that acts as a barrier to reduce friction, wear, metal scoring and eliminates the possibility of welding.<sup>1</sup>

The fourth extreme pressure additive type, overbased sulfonates, operates by a different mechanism. This species contains a colloidal carbonate salt dispersed within the sulfonate. During the interaction with iron, the colloidal carbonate will form a film that can act as a barrier between metal surfaces. This process is not dependent on temperature as compared to those with chlorinated, sulfurized and phosphorus-based additives. It is reported that the carbonate film will form at temperatures below 500 C.<sup>2</sup>

### Examples of EP additives

Within each category of EP additive, there are several different types of additives. For example, the main chlorinated additive used is chlorinated paraffin, which is available at a number of different percentages of chlorine. Other commercial types include: chlorinated olefins, chlorinated fatty acids



and chlorinated esters.

In the case of phosphorus compounds, the main type employed is phosphate esters. But two other functionalities used are phosphites and phosphonates.

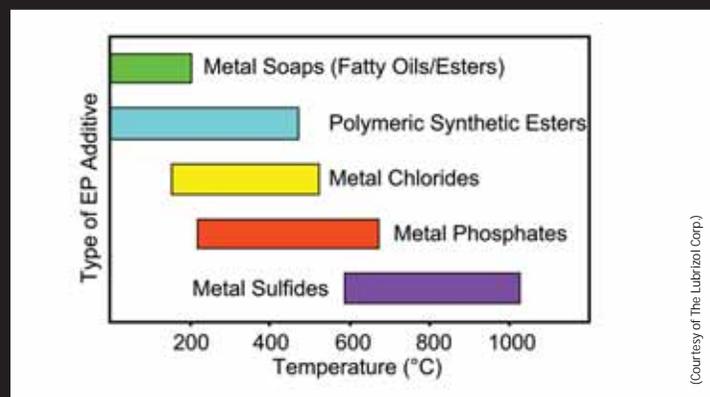
The following types of sulfurized additives are available: sulfurized greases, sulfurized esters, sulfurized hydrocarbons and polysulfides. Depending upon the processing, these additives are available as either dark-colored or light-colored species. Sulfurized additives also are differentiated by the concentration of active (or free) sulfur present. Active sulfurized additives will stain copper alloys to some extent. Formulators are urged to evaluate these additives in their products for staining by using the ASTM D-130 procedure.

Overbased calcium and sodium sulfonates are used as EP additives. The total base number (TBN) for these additives ranges from 300 to 400.

CONTINUED ON PAGE 12

The operating temperature ranges are shown for chlorinated, phosphorus-based and sulfurized EP additives. These ranges are compared to the operating ranges for traditional boundary lubricity additives and polymeric esters.

Figure 1. Activation Temperatures for Various EP Additives



(Courtesy of The Lubrizol Corp.)

## EP additive trends

Representatives of the five EP additive manufacturers spoke to TLT to provide a feel for how their products are being used and why EP additives are so important to the lubricant formulator.

Achim Fessenbecker, vice president, head of technology lubricant oil additives for Rhein Chemie Rheinau GmbH (a supplier of sulfurized additives, phosphate esters, dithiophosphates, sulfur/nitrogen compounds, overbased sulfonates and combinations of these additives) says, "EP additives can be used in all types of tribological situations to minimize machine wear. Key applications

include gear oils, greases, hydraulic fluids and metalworking fluids."

STLE member Frank Kroto, global technology manager for The Lubrizol Corp. (a supplier of sulfurized additives, phosphate esters and overbased sulfonates) says, "EP additive use is formulation and application dependent. For severe metal removal applications such as tapping, reaming and broaching (see

Figure 2) and metal forming operations, EP additives provide the needed performance features to minimize metal-to-metal contact and improve tool life."

Kroto indicated that EP additives may not be required in some cases where the temperature at the point of machining does not rise sufficiently to activate a specific additive. An example of where this comes into play is the use of water-soluble sulfurized additives. In less severe applications, they would not be activated because of the high level of water present at the

use dilution. But Kroto finds that water-soluble EP additives are effective in severe applications when formulated into semisynthetic metalworking formulations, particularly in drawing and stamping.

Fessenbecker adds that formulations based on sulfurized additives can be effective in machining soft metal alloys (e.g. aluminum) that do not reach the activation temperature. He says, "We have found that sulfurized additives are useful in the processing of soft aluminum alloys. This can occur both with neat oils and with water-dilutable fluids."

STLE member Curtis Lege, business unit manager, lubricant additives for Dover Chemical Corp. (a supplier of chlorinated additives, sulfurized additives, phosphate esters & phosphites and overbased sulfonates) says, "One important feature in working with EP additives is to utilize those chemistries that contain a fatty group. The fatty group provides lubricity and improves the ability of the EP additive to remain adsorbed on the metal surface during use. In the case of a chlorinated fatty derivative, chlorine can be released more readily from the carbon atom next to the carbonyl group than in chlorinated paraffin. This leads to improved EP performance."

STLE member Charles Aymes, business development manager, industrial/metal treatment for Rhodia Inc. (a supplier of phosphate esters, phosphites and phosphonates) says, "The chemistry of the EP additive can be adjusted to optimize performance. Phosphate esters are prepared as a mixture of mono- and diesters (see Figure 3). The ratio of these two components can be adjusted to maximize performance depend-

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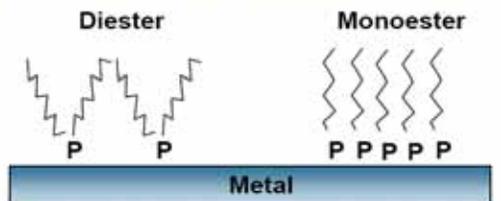


Figure 2.

Broaching of gears is a severe metal removal operation that requires the use of metalworking fluids formulated with EP additives.

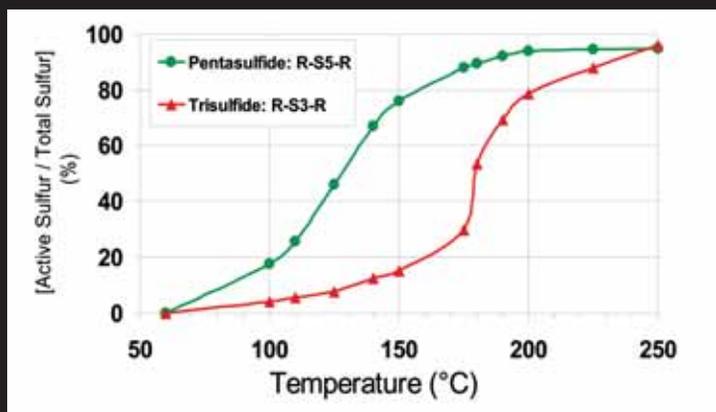
Figure 3. The Chemistry of Phosphate Esters

Phosphate esters can be tailored to meet EP requirements by optimizing the mono to diester ratio



The structure of phosphate esters can be tailored to meet the requirements of the end-use application. Phosphate esters are a mixture of mono- and diesters.

Figure 4. Combining EP Additives: Performances controlled by molecular architecture



(Courtesy of Arkema Inc.)

Sulfurized additives can be prepared with trisulfide and pentasulfide structures. Thermal stability differences between these two types leads to their use in different applications.

upon the application.”

Phosphonates can provide excellent performance under high-temperature conditions because of their enhanced thermal stability. Aymes adds, “Phosphonates are also more hydrolytically stable because they contain carbon-phosphorus bonds as compared to carbon-oxygen-phosphorus bonds present in phosphate esters.”

Francois Court, global lubricant market manager for Arkema Inc. (a supplier of sulfurized additives and phosphate esters) says, “The consistency of the EP additive, which is linked to the manufacturing process, is very important to ensure optimized performance. Other factors to consider are the chemical stability, thermal stability, solubility in basestocks and odor.”

The structure of a sulfurized additive has an impact on its use in specific applications. During the preparation of a sulfurized additive, the number of sulfur atoms that become incorporated into the molecule can be controlled. Typically, commercial additives are centered on either three or five sulfur atoms that are known

as trisulfides and pentasulfides, respectively.

Court says, “There is a difference in thermal activity between trisulfides and pentasulfides as the temperature is increased from 60 C to 250 C (see Figure 4). An increase in temperature leads to the generation of more active sulfur. Trisulfides release active sulfur at a slower rate and at higher temperatures than pentasulfides. Pentasulfides, thus, are well suited to low-speed, high-torque metalworking operations where sulfur must be readily available. Trisulfides are best used in higher speed metalworking operations and also in applications such as automotive and industrial gear oils where the release of sulfur shall not be detrimental to these systems.

### Interactions with other additives

Kroto indicates that determining how to use EP additives in combination with other additives is based on the machining operation, metallurgy, tooling, set-up and the desired performance. He says, “One of the most important aspects for the formulator to consider is the potential for premature tool failure before the operation reaches the proper temperature and the EP additive can be activated. This requires the need for a boundary lubricity additive that will work synergistically with the EP additive.”

Differences in the choice of boundary lubricity additives require that formulators evaluate their chemistry and the application before making a selection. Kroto adds, “Higher molecular weight polymerized esters display superior thermal and oxidative stability compared to other types of esters. This characteristic coupled with their higher viscosity gradient enables polymeric esters to maintain a film on the metal surface at higher temperatures.”

Another example of a synergistic combination was cited by Fessenbecker. He says, “We are always looking to find additive combinations that will boost lubricant performance. In laser-guided tool operations, we have found that formulating light-colored sulfurized additives with polymeric esters leads to superior performance without the need to clean the part.”

Aymes indicates that it is difficult to select a specific additive because the formulator has an infinite number of choices. He adds, “In formulating lubricants, the challenge is not just to find synergistic combi-

nations but also to minimize unfavorable interactions that can result in product instability and foam generation. The best approach is to utilize multifunctional additives to simplify formulations.”

Lege stressed that the combination of chlorinated and sulfurized additives is very helpful to the formulator, especially in heavy-duty applications. He says, “It is very useful particularly to use both chlorinated and sulfurized additives in heavy-duty drawing operations.”

Court indicated that synergisms also can be found with other combinations of EP additives. He says, “We found experimentally that synergisms can be obtained between sulfurized additives, phosphorus-based components and overbased sulfonates. Of course, the synergy between sulfurized and chlorinated additives also is well documented.” The use of specific additive combinations is dependent upon the application.

### **Why are EP additives so important?**

In response to the STLE survey, the five representatives were asked about why the lubricant industry sees the importance of

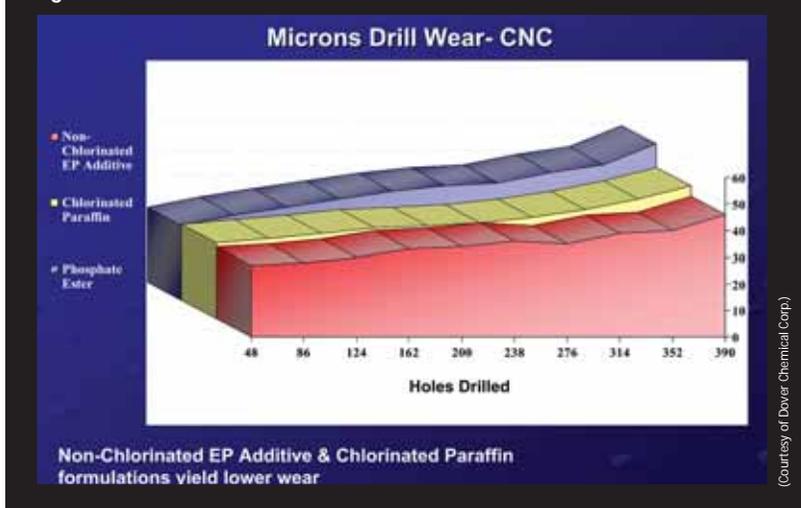


EP additives in their products.

Court says, “The tough competitive nature of lubricant applications requires end-users to push product performance beyond the limit. The lubricant user will save money by extending tool life, reducing energy costs and operating its machinery at higher speeds. All of these technical limits are

**CONTINUED ON PAGE 16**

Figure 5. Non-Chlorinated EP Additive



In the drilling of 316 stainless steel, neat oils formulated with the non-chlorinated EP additive and chlorinated paraffin displayed comparable results. Slightly inferior results were found with a neat oil formulated with a phosphate ester.

'extended' by adding EP additives. EP additives are required to enable the lubricant to operate beyond its designed limits."

Lege adds, "EP additives enable lubricants to exhibit superior load bearing properties which leads to extended tool life in metalworking operations and gear life in industrial machinery." Aymes indicates that the importance of EP additives is due in part to the restricted number of choices available to the formulator. "Formulators may be willing to sacrifice other lubricant properties such as foaming, but EP is essential because it is directly responsible for ensuring that a specific metalworking operation will succeed," he says.

Fessenbecker says, "Additives formulated into lubricants provide different properties to enable machinery to function at an optimum performance level. While other additives are used to protect the specific lubricant, EP additives are needed to protect the machinery doing the specific operation. This may include the cutting tool, machine tool and workpiece in metalworking. The stronger demands

on gearboxes require the use of EP additives in gear oils to ensure long operating intervals."

Kroto summarizes the importance of EP additives: "There are some operations in which EP additives absolutely must be used in order to get the job done."

### EP additive trends

During at least the past 20 years, there have been many discussions and some regulations enacted to limit the use of chlorinated paraffins. The industry representatives contacted for this article believe in general that the use of chlorinated paraffins will drop, but there is no clear indication about how rapid the rate of decline will be.

Lege says, "We see that chlorinated paraffin use is a little bit at risk. Types such as medium chain and long chain chlorinated paraffins have been around for a long time and will continue to be used at current levels for at least the next five years."

Fessenbecker also sees chlorinated paraffin use in decline and believes there is a technical concern. He says, "We see that the use of chlorinated paraffin-based metalworking fluids in high-speed machining operations is leading to shorter activation times. This can produce higher quantities of hydrogen chloride which will produce corrosion problems and reduce tool life."

Kroto sees different regulatory standards governing the use of chlorinated paraffins worldwide. He says, "Determination of chlorinated paraffin use is made on a country-by-country basis. Formulators have to decide how to use chlorinated paraffins to position their product lines from both a regional and worldwide perspective."

One driver that will impact the use of all additives in lubricants is the new regulation system known as REACH that was established in the European Union (EU) in December 2006. The EU considers the most widely used chlorinated paraffin type, known as medium chain chlorinated paraffins, to be toxic to marine life. Appropriate risk phrases (R50/R53) are included on manufacturers' MSDS.

This places chlorinated paraffins in the category of "chemical substances of high concern." In the future, EU authorities may prompt manufacturers of chlorinated paraffins to commercialize safer alternatives.

There is a great deal of uncertainty about

REACH at present. Further information can be found in a feature article in this issue of TLT.<sup>3</sup> All of the EP manufacturers contacted for this article expressed the commitment to register their products in REACH.

Research is continuing to learn more about how EP additives are used and to develop new technologies. Lege says, "We have developed a new product that we call a non-chlorinated EP additive. Evaluation of this technology shows good performance on very hard alloys such as stainless steel and hastelloy. We have also observed good results on titanium, which can be very difficult to machine and cannot tolerate chlorinated additives due to concerns about stress cracking."

The non-chlorinated EP additive does not contain any chlorinated, sulfurized or phosphate-based components. Lege indicated that this new additive can work in a synergistic fashion with other EP additives. In a recent study, comparable results were found when using neat oils based on chlorinated paraffin and the non-chlorinated EP additive to drill 316 stainless steel. Both fluids also contained a sulfurized additive. Slightly infe-



rior results were observed with a fluid containing the same sulfurized additive and a phosphate ester (see Figure 5).

Aymes indicates that Rhodia is looking to develop new phosphate ester technologies that generate lower levels of foam. He adds, "We are also looking at customizing our phosphonates to provide good EP proper-

**Editor's Note:** See page 30 for TLT's in-depth feature article on the EU's REACH regulations.

CONTINUED ON PAGE 18

ties and stain-free surfaces.”

Fessenbecker says research efforts are directed toward more environmentally friendly EP additives. He says, “We are looking to develop a portfolio of biodegradable products. Other areas of emphasis include boosting the solubility of EP additives in the latest generation of base oils (Group II, Group III and Group IV) and improving their thermal stability.”

Kroto indicates that Lubrizol will continue to broaden its product line. He says, “We added sulfurized vegetable oils two years ago, and we are looking to develop new products with better aesthetics (color and odor) in combination with superior performance.”

Court says, “We have recently developed a water-soluble sulfurized additive that can

be used in semisynthetic and synthetic metalworking fluids to boost performance in specific applications. In the future, additives that will provide flexibility to the formulator will be desirable.”

All industry representatives interviewed feel that regulatory drivers will have a major impact on the future use of EP additives. But making further predictions about changes in the offerings of EP additive technologies either in the near or long term is difficult.

Fessenbecker says, “The lubricant industry is very conservative, and we do not see any major changes over the long term. There will be a steady evolution in which EP additive technology will be adjusted. Solid EP additive use will increase, and this will include finely dispersed nanoparticles that are being developed in the relatively new field of nanotechnology. There also will be a greater need for EP additives with better thermal stability.”

Court believes there will be a move toward more efficient metalworking fluids in part because of regulatory drivers such as REACH. He adds, “This will prompt further interest in the use of high-performing additives because of the need to reduce waste. We see sulfurized technology as a key contributor (or cornerstone) to this evolution, together with the development of dry lubrication.”

Aymes agrees that more efficient lubricant and EP additives will be required in the future. He says, “Incorporation of more than one EP additive chemistry on a molecule (hybrid) and the use of gemini surfactant technology could be promising in the development of new products. But EP additive use could be reduced with the greater use of wear-resistant coatings on cutting tools.”

Lege says, “It is tough to determine how EP additive technology will evolve in the future. There are too many variables involved such as workpiece alloys, cutting tool technologies (coatings) and wastewater treatment. EP additive manufacturers must quickly react to these changes in order to have products available to meet these needs.”

Kroto believes that EP additive suppliers will be challenged to develop new products that can be used to machine a wide variety of alloys. He says, “Formulators are faced with developing products for more difficult-to-machine alloys. This will place a premium on using the right types of EP additives in the metalworking fluid formulation to machine parts that meet increasingly tight specifications.” <<

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