The Future of Metalworking Fluid Additives

Formulators in the U.S. and Europe respond to the challenge of ever-tightening government regulation.

BEING A METALWORKING FLUID FORMULATOR is becoming as complex as metalworking fluids (MWF) themselves. While MWF formulators face many of the same cost/benefit challenges of other lubricant developers, they have additional issues that stem from the close regulatory scrutiny of MWFs in the workplace.

STLE member Alan Eckard, vice president of technology for Monroe Fluid Technology, explains, "The GHS[1] (Globally Harmonized System) regulations, which will be in full force by mid-2015, will have significant impact due to compliance difficulties and end-user pushback on new hazard warnings that in many cases look more onerous than they have in the past. In addition, REACh[2] registration requirements in Europe will effectively preclude shipment of most MWF additives from outside the Euro-zone unless the supplier already has substantial volumes either coming in or produced in the EU, which would justify registration."

Eckard concludes, "The cost of participation in the consortia is very high. Many additive suppliers outside (and a significant number inside) the EU do not realize

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that even if a substance is registered or preregistered by others, anyone making the additive or importing it needs to participate in the appropriate consortium and pay their share of the registration costs."

In order to work well in an array of metalworking applications, MWFs usually contain more additives than other lubricants. MWFs provide lubrication and cooling but also facilitate chip removal. Many metalworking processes create fresh surfaces. If these freshly generated surfaces are not covered by a lubricant immediately, welding between the workpiece and tool (sticking) occurs. MWFs play a critical role in protecting both the workpiece and the tool.

While dry machining is adequate in some operations, most often the absence of MWF cooling and lubricating properties would result in faster tool wear, residual stress and workpiece defects. For today's demanding machining challenges, such as milling ultra-high-strength steels, the use of metalworking fluids is critical. Ultimately MWFs prolong tool life, improve workpiece quality and expedite manufacturing.

There are four basic classes of MWFs:

1. **Straight oils.** Composed of mineral, animal, marine, vegetable or synthetic oils. Straight oils are not diluted with water, but other additives may be present.
2. **Soluble oils.** Containing anywhere from 30-85 percent ultra-refined mineral oils and emulsifiers to dissolve the oil in water.
3. **Semisynthetic fluids.** Containing 5-30 percent ultra-refined[3] mineral oils, 30-50 percent water and the remainder additives.
4. **Synthetic fluids.** Containing no mineral oil.

Semisynthetic fluid is difficult to formulate because it contains high percentages of both mineral oil and water. This creates a multitude of solubility and compatibility issues between the base oil and additives.

COMPARATIVE LIFECYCLE ASSESSMENT OF GAS-BASED AND WATER-BASED MWF SYSTEMS[4]

In the move toward sustainable manufacturing, informed MWF selection is not possible without systematically considering lifecycle impacts of alternative system approaches. To that end, researchers at the University of Michigan, University of Virginia and Purdue University created a lifecycle assessment (LCA) model of MWF emissions that included the material production phase, use phase and disposal phase for four metalworking fluids: a semisynthetic microemulsion of petroleum oil in water, a semisynthetic microemulsion of rapeseed (canola) oil in water, a petroleum oil in air MQL spray and a rapeseed oil in CO_2 MQL spray.

The model was designed to capture variations in MWF delivery—recognizing that MWF usage varies significantly by operation and by operator preference. The functional unit for the study was the amount of MWF required to run one stand-alone machine tool for one year; additional impacts from centralized MWF systems were not considered. Also the impacts of tool production were not included.

Results showed that tradeoffs exist across the impact factors although there is one clear trend: The environmental impacts of the gas-based lubricant systems are generally lower than the water-based lubricant systems. Although the gas-based systems are somewhat higher in global warming potential (GWP), the total greenhouse gas emissions from all MWF systems was relatively small, at most about a fifth of the GWP emitted from the tailpipe of an average automobile per year.

COMMON MWF ADDITIVES

The 12 common MWF additive categories include:

1. Sulphurized or chlorinated compounds
2. Corrosion inhibitors
3. Extreme pressure additive
4. Antimist agents
5. Emulsifiers
6. Alkanolamines
7. Biocides
8. Stabilizers
9. Dispersants
10. Antifoamers
11. Colorants/dyes
12. Fragrances.

In some cases, more than one additive of a category is required—for example, two different biocides in the same formula.

One of the most difficult to formulate additives is the antifoam agent. These additives operate on the boundary between the air and the fluid and often will either rise to the top of the fluid or sink to the bottom, or they will become too soluble leaving the boundary area between the air and the fluid exposed. The goal for formulators is to ensure that the antifoam agent will remain compatible with a particular metalworking fluid formulation and retain its properties for a long time. This is difficult to achieve because antifoam additives tend to deplete quickly—necessitating an additional antifoam additive while the MWF is in use.

ENVIRONMENTAL AND HEALTH EFFECTS OF MWF ADDITIVES

Several additives have been eliminated from use in MWFs, including nitrites and short-chain chlorinated paraffins. There is a growing pressure to further eliminate additives that may be harmful to the worker or the environment. Other additives such as medium-chain chlorinated paraffins are under scrutiny; some experts believe they may be banned soon, but Dover Chemical is not one of them. The company's official stance states, "Chlorinated paraffins (CPs) have been under review for several years now with no restrictions implemented on medium-chain CPs thus far. Further review of chlorinated

paraffins will continue into 2015 and possibly beyond."

A typical water-based MWF will contain water, oil, surfactants and about 10 other additives. These MWFs require maintenance technologies such as depth filtration, centrifugation and biocide application to delay deterioration. This deterioration leads to microbial growth and health risks, and eventual disposal.[5] The deterioration of these MWFs arises from many sources such as:

Ultimately MWFs prolong tool life, improve workpiece quality and expedite manufacturing.

- The fundamental incompatibility of oil and water
- The susceptibility of emulsions to microbial growth
- The evaporation of water
- Hard water ions that destabilize emulsions
- The susceptibility of surfactants to foam when mechanically agitated.[6]

As these factors also facilitate microorganisms, protecting the machinery also protects worker health and ultimately the environment. Improving the eco-friendliness of water-based MWFs depends on:

1. Selecting an environmentally benign (bio-based) MWF chemical formulation. In addition to protecting worker health, bio-based MWFs will reduce waste treatment costs.
2. Instituting an appropriate control system for the formulation that maximizes the MWF lifespan.

THE ENVIRONMENT AND REGULATIONS

In the STLE textbook *Metalworking Fluids*, Eugene M. White writes; "MWFs are difficult to classify and regulate due to their chemical diversity and proprietary compositions. Chemical regulations are usually applicable to pure chemical substances or defined compounds that can be sampled and analyzed by scientifically validated methods. Another barrier to the regulation of MWFs is that, during normal usage, they undergo physical, chemical and biological changes. Thus, it is not always clear whether regulations address issues caused by the inherent properties of unused fluids, changes that occur in used fluids or extrinsic conditions in the fluid/machining environment."[7]

It's difficult to regulate MWF base oils and additives that are either nontoxic or are low toxic in their nature state.

Craig Mott, vice president of Colonial Specialty Chemical, says, "Biocides—formaldehyde-release chemistry, CPs (chlorinated paraffins), boric acid-based products, NPEs—basically anything currently on the TSCA Chemicals of Concern List, anything that has been given a TSCA New Use Rule and anything that shows up on the TSCA Work Plan for Chemical Assessments will be affected by environmental regulations. Moly-based products were just added in 2014 to the Work Plan List, which means they could be under heavy scrutiny next."

DISPOSAL

The primary disposal options for plants are contract hauling or treatment for sewer disposal. What precipitates disposal is a combination of biological growth, property changes of the MWF in use and contaminants such as metal (cobalt and lead). Disposal of decidedly eco-*unfriendly* additives and metal-laden MWFs is usually both difficult and expensive.

MWFs released directly into wastewater can overload sewage treatment systems and may contain components that ordinary treatment systems cannot handle. Facilities that discharge wastewater to municipal sewage treatment systems are required to pre-treat MWFs until levels of key characteristics are below specified limits, which are generally set by municipalities operating the sewage treatment plants and subject to local, state and federal laws.

In some instances, MWFs must be handled as hazardous waste—either because of materials present in the fluid as purchased or because of materials that become mixed with the fluid during the machining process. Since managing hazardous waste is expensive and labor-intensive, avoiding the hazardous classification in the first place is the best compliance option.

A viable alternative to conventional MWFs (and their additives) are environmentally adapted lubricants. EALs are highly biodegradable and have comparatively low toxicity. Important-

BEST PRACTICES FOR PREVENTING HAZARDOUS WASTE[8]

The following considerations may help minimize the quantity of waste MWFs needing disposal:

- When choosing which fluids to use for a particular application, look at entire lifecycle costs, including fluid lifetime and treatment and disposal costs.
- Establish a maintenance schedule that includes checks on fluid chemistry and concentration, contamination levels (including dirt, tramp oils and biological growth) and odors.
- When fluid is to be diluted with water, use good quality water. An ion exchange system or reverse osmosis unit may be a worthwhile investment for prolonging fluid life.

ly, in order to receive that designation, they must perform equal to or better than conventional alternatives. About 5 percent of all lubricants in the EU are now being sold as EAL oil-in-water emulsions, primarily as vegetable-based formulations, and their market share is growing.

Minimum quantity lubrication (MQL) techniques represent another growing class of EALs. MQL typically involves sprays of compressed air and a small amount of oil to provide the function of an MWF without the large amount of waste. The limitation of MQL systems is that they don't cool well, so they are only suitable for low-speed, low-impact machining operations that do not require significant heat removal. Current research is focused on developing new approaches that extend the applicability of MQL to more demanding machining processes.[9]

MWF ADDITIVES AFFECTED BY NEW REGULATIONS

According to John Nussbaumer, Dover Chemical's technical service manager for metalworking, future regulations regarding MWFs will most likely affect the area of chlorinated paraffins (CPs). Chlorinated paraffins, which are a staple of the metalworking fluid industry, work in a wide range of metalworking applications in both water-based and oil-based formulations. There are currently four classifications of CPs:

- **Short-chain.** Those with a carbon chain distribution <14
- **Mid-chain.** Those with a carbon chain distribution of 14-17
- **Long-chain.** Those with a carbon chain distribution of 18-20
- **Very long-chain.** Those with a carbon chain distribution that is >20 (this is a new classification).

"We have already seen short-chain CPs eliminated from use in MWFs," Nussbaumer says. "Currently the mid- and long-chain CPs are under review. However, it does not appear that any action will be taken on either classification in the near to midterm. The main focus on mid-chain CPs likely will center on the amount of short-chain olefin that is present in C-14 alpha olefin when it is produced. The content of short-chain olefin is already typically <1 percent. Very long-chain CPs will be reviewed at a later date, but it does appear that no action will be taken on very long-chain CPs."

HEALTH EFFECTS

MWFs are vulnerable to microorganism contamination. This can create direct health risks for workers from infection, inhalation of bio-aerosols and indirect risks from skin contact with biocides used to control the microorganisms. Some 1.2 million workers in machine finishing, machine tooling and other metalworking and metal-forming operations are potentially exposed at any time.[10]

Skin and airborne exposures to MWFs have been implicated in irritation of the skin, lungs, eyes, nose and throat. Conditions such as dermatitis, acne, asthma, hypersensitivity pneumonitis, irritation of the upper-respiratory tract and a variety of cancers have been associated with exposure to MWFs.[11] The severity of health problems is dependent on factors such as the kind of fluid, the degree and type of contamination and the level and duration of the exposure.[12]

Two types of skin diseases associated with MWF exposure are acne and contact dermatitis. People working with water-based, synthetic and semi-synthetic MWFs are most at risk for developing contact dermatitis.

Inhalation of MWF mist or aerosol may cause lung, nose and throat irritation. In general respiratory irritation involves some type of chemical interaction between the MWF and the human respiratory system. Exposure to MWFs has also been associated with asthma. Work-related asthma is one of today's most prevalent occupational disorders, leading to significant costs in healthcare and workers compensation.[13]

Studies that may not be relevant today have suggested an association between working with MWF chemistry and practices that were phased out decades ago and certain cancers.[14] Because of a demonstrated latency period, these studies have relied on health reports of workers exposed decades earlier when airborne concentrations of MWFs were much higher than they are today. The composition of MWFs also has changed dramatically over the years—with many chemicals (i.e., nitrite) since removed because of health concerns.[15,16]

Mick Wragg, senior global product steward for The Lubrizol Corp., says, "The recent publication in the U.S. by The National Toxicology Program[17] on the adverse effects of long-term inhalation exposure to a commercially available fluid will no doubt lead to further questions about metalworker health associated with inhalation exposure to cutting fluids. It will also be interesting to see what short- to medium-term impact the recently announced changes to chemical control legislation in Taiwan and Korea will have on the Asia-Pacific region."

THE PARTICULAR PROBLEM OF BIOCIDES AND CHLORINE

Without biocides, water-based MWFs would be breeding grounds for bacterial and fungal organisms. These organisms would lead to metabolic destruction of some active ingredients and reduce MWF performance. While ordinary microbes pose little infection risk for workers, particularly hazardous species have caused worker illness. Thus, water-based MWFs require biocides to curb these organisms. No one would argue that biocides are effective. The goal is to minimize biocides because excessive concentrations carry their own health risks, ranging from acute dermatitis to more severe conditions.

Heat pasteurization and ultraviolet irradiation would be viable alternatives to biocide use if these processes were not significantly more expensive. Membrane filtration is another alternative. One of the key factors in effectiveness is having an embedded sensor to detect microorganisms when they begin to form.

Fluids that contain biocides are regulated under federal rules that apply to a number of substances, including pesticides. Triazine-based biocides used in metalworking fluids are members of a larger class of antimicrobials prepared by reacting an amino alcohol with formaldehyde.

As a result of many years of proven use, triazines have been shown to be highly effective, cost-effective chemical compounds. Recently the efficacy of using triazine-based and similar antimicrobials has come into question because of concerns about their ability to control a particular organism (*mycobacterium*). Certain species of mycobacteria are thought to be causative agents of—or at least strongly associated with—hypersensitivity pneumonitis in workers exposed to MWFs in certain working conditions.[18]

"The alkylphenol ethoxylates are largely being phased out of MWFs and several alternatives are available based on alcohol ethoxylates," Eckard says. "There is particular concern about formaldehyde-releasing biocides and increased concern with borate-type chemistry. Avoiding formaldehyde releasers is troublesome, but alternative materials that cost more to use are available. Borate chemistry is very cost effective and multifunctional so replacement is just going to increase cost."

Extreme pressure (EP) additives typically contain organic sulfur, phosphorus or chlorine compounds, including sulfur-phosphorus and sulfur-phosphorus-boron compounds, which chemically react with the metal surface under high-pressure conditions. And CPs are under close scrutiny.

John Nussbaumer, Dover Chemical's technical service manager for metalworking, explains, "Some of our most successful chlorinated alkane alternatives have been commercial for over 20 years. This development was driven primarily by customers who wish to formulate away from CPs. Such additives are based on polyolesters, sulfur, phosphorous, sulfurized overbased sulphonates and nitrogen. Chlorinated esters and fatty acids also work very well as CP alternatives as they are biodegradable but still contain chlorine within their backbone."

He continues, "While we have been successful in replacing chlorine in specific operations, we have found that alternative chemistries are not necessarily drop-in replacements across the board for CPs. Chlorine is unique as it has the broadest operating temperature of all EP additives. This broad operating temperature is one of the properties that allow chlorinated paraffins to be so versatile. Chlorinated paraffin alternatives can be used in a multitude of applications. Many times, the results when using chlorinated paraffin alternatives are equal to or better than the results when using only CPs. The main issue when using chlorinated paraffin alternatives is that they don't cover the wide variety of applications that CPs alone can cover. This means that an end-user may have multiple formulations when using CP alternatives as opposed to one formulation when using CPs only."

AN INTERVIEW WITH LOU HONARY ON BIO-BASED MWFs

Lou Honary is chairman and president of Environmental Lubricants Manufacturing, Inc., in Grundy Center, Iowa, and a recognized expert on bio-based fuels and lubricants.

Are there special considerations regarding bacterial growth in bio-based MWFs?

The working of biocides in bio-based metalworking fluids is different than those of conventional metalworking fluids. In the case of bio-based MWFs, if the base oil is vegetable oil, then the base oil itself could act as food for bacteria and would require more diligent monitoring. But the extra effort to maintain the bio-based MWF pays off with the improved performance and significant cost savings.

But what about the health effects of biocides?

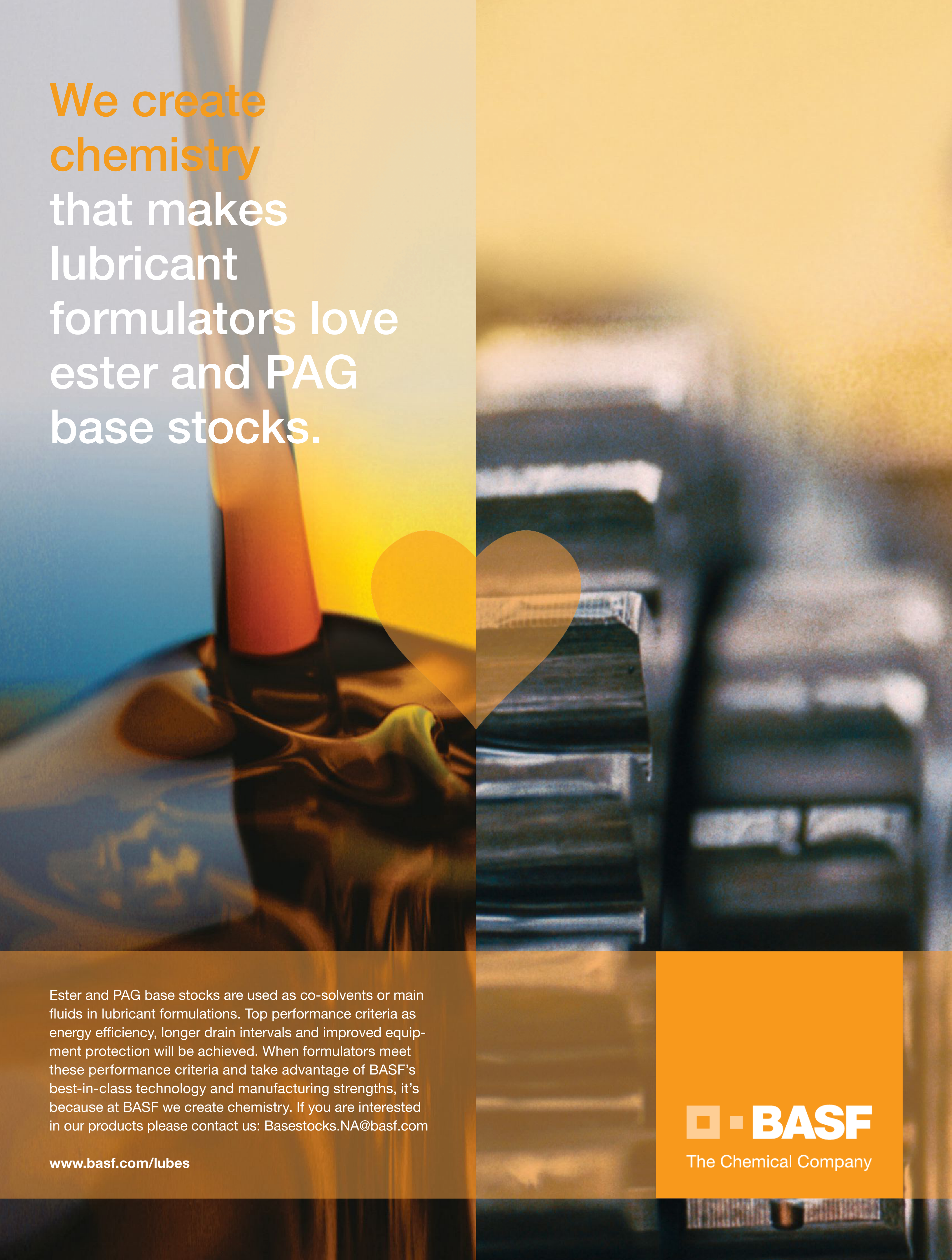
Our experience has been that excessive use of biocides impact the end-user negatively regardless of whether the base oil is bio-based or mineral oil-based. It will be important to see how the evolution of bio-based metalworking technology affects the end-user in the future.

How well do additives perform in bio-based MWFs?

In my experience, many of the same additives used for mineral oil-based MWFs work for bio-based products as well. The vegetable oil-based versions of bio-based MWFs can also benefit from the experiences of the food industry, which is mature in handling foodstuffs and protecting them from bacteria by adding a large number of natural chemicals. I believe that as the market for bio-based MWFs grows, more of the natural food preservatives and biocides will migrate from the food industry into metalworking applications. We have no reservations about the field performance of bio-based MWFs with current biocides and chemical additives.

Anything else that you would like to add?

I believe ultimately, the success of bio-based MWFs and their additives will depend on the current manufacturers and marketers of MWFs and MWF additives—when they accept that there is great opportunity in selling these products along with conventional MWFs.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Nussbaumer concludes, "Another issue with CP alternatives is appearance. The vast majority of CPs are very light in color. Most of the CP alternatives have an ASTM color that is darker. This becomes an issue when the end-user needs to see what is happening at the tool/workpiece interface. Another area where CPs are more effective than their alternatives is cost. There is currently no cost-effective CP alternative offered to the market."

Mott agrees, "In many cases the alternative chemistries are not as effective and/or are higher cost and can be much more difficult to formulate with. The industry has long struggled with chlorine replacement technologies, which simply cannot perform as well as chlorinated paraffins on certain alloys and applications. Chlorine replacements are almost always more expensive on a treat-rate basis and cannot replace chlorine in all applications."

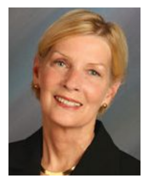
Wragg adds, "Increasingly, we are seeing certain classes of metalworking chemistry being targeted by regulators and downstream users as a result of classification and labeling legislation, especially in the European market. Specifically there are two types of chemistry included in this: formaldehyde-releasing biocides where the concern is associated with the carcinogenic potential of released formaldehyde and boron-containing ionic compounds where the concern is associated with the alleged reproductive hazard of boric acid."

WHAT IS TO COME FOR MWF ADDITIVES?

Government regulation of MWFs (particularly their additives) is almost certain to tighten. This creates a conundrum for formulators who need to produce fluids that perform well for extended periods and also protect the machinery, workpiece, environment and most of all the workers. And these MWFs need to do all this at a cost that is palatable in the marketplace.

Eckard concludes, "There are options, but cost is the real issue. Especially with antimicrobial materials, making them so benign that most label warnings and most health hazards are gone leaves a relatively ineffective product."

Nussbaumer says, "Right now at Dover Chemical we are focusing on synergies. When we talk about synergies, we are looking at the combination of additives to enhance the performance of a fluid. We do not see the use of mid-chain chlorinated paraffins being affected by regulations in the near to mid-term. We see the use of long and very long-chain chlorinated paraffins continuing for the foreseeable future. Prior to any new regulations restricting their usage, additional research and evaluation will be required to determine whether such regulation is necessary." **TLT**



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