KEY CONCEPTS

• Formulators are taking a hard look at formaldehyde-releasing biocides—partly because of looming regulations and partly because of consumer demand.

• While no agency has banned all formaldehyde-releasing biocides, formulators are seeing a trend in that direction.

• Eliminating biocides is not the answer as microbes proliferating in the absence of biocides also have health consequences.
Science, regulators and formulators seek ways to maintain industrial production while ensuring worker safety.

While formaldehyde-releasing biocides have been around for a long time, ever more stringent regulatory pressures have been forcing formulators to investigate alternative chemistries.

**ILLNESS ACCOUNTED FOR THE VAST MAJORITY OF ALLIED CASUALTIES** during the Pacific Campaign in World War II, with mosquito-borne malaria being the main problem. Although most soldiers survived, in some areas entire units were immobilized for weeks at a time.

In 1947 health agencies around the world began an aggressive campaign to eradicate malaria, with the primary weapon being DDT. By 1949 the U.S. was declared free of malaria as a significant public health problem.1,2,3

Two decades later, DDT—once the miracle savior—was the whipping boy for everything that was wrong with the indiscriminate use of toxic chemicals. It’s a similar (although scaled down) situation with formaldehyde-releasing biocides in metalworking fluids (MWFs)—they both solve and create health problems.

MWFs are essential for maintaining the tool and surface temperature and maximizing the life of the tool by lubricating the cutting tip and preventing corrosion (see Types of MWFs). During the metalworking process, the MWF floods and cools the work surface. The used, heated coolant then flows off for everything that was wrong with the indiscriminate use of toxic chemicals.

**TYPES OF MWFs**

There are five basic categories of MWFs. Solubles, semisynthetics and synthetics are sold as concentrates and then diluted with water at the point of use. Due to their water content, they are naturally more susceptible to biological infiltration.

1. **Straight oils**, which are used without dilution and composed of mineral, animal, marine, vegetable or synthetic oils
2. **Soluble oils**, containing anywhere from 30%-85% ultra-refined mineral oils and emulsifiers to allow dilution in water
3. **Semisynthetics**, containing 5%-30% ultra-refined mineral oils, 30%-50% water and the remainder performance additives
4. **Synthetics**, which contain only water and water-soluble additives but no mineral oil
5. **Biobased versions of the first four**: formulated with refined-bleached-deodorized vegetable oils or biobased-derived synthetic esters.
the surface into a collection container (sump) where it cools off and then enters the cycle again.

Metalworking fluids come in the form of straight oil that are fortified with additives that help to reduce friction and tool wear, and in the form of water-emulsified coolant that are usually a mixture of water and oil. It is typically the coolant that requires a significant amount of biocides and an environment that is hostile to bacteria. The deterioration of MWFs arises from many sources, such as:

- The incompatibility of oil and water
- The evaporation of water
- Destabilizing hard water ions
- The susceptibility of surfactants to foam when agitated
- The susceptibility of emulsions to microbial growth
- Introduction of foreign matter including bacteria from the operator or operation environment.

**MICROBES**

Microbes thrive in the environment created by MWF impurities. They feed on mineral oils, fatty acids, emulsifiers, corrosion inhibitors, other additives and waxes in oil-based and synthetic coolants. For example, they consume the corrosion inhibitors in synthetic coolants—aerobic bacteria require oxygen for metabolism and efficiently destroy the coolant. Anaerobic bacteria grow in environments lacking oxygen. They feed on the coolant and produce noxious by-products such as hydrogen sulfide.4

Microbes also can expose workers to pathogens and contribute to respiratory and skin irritation (see The Difficulty of Measuring Microbes). They decrease workpiece quality, resulting in surface blemishes, decreased tool life and increased downtime to treat bacteria and repair equipment. The microbes also can increase foaming and oil separation and clog lines, filters and valves.5

Like all lubricants—regardless of the formulation—all MWFs eventually deteriorate. But the fluid itself is not inherently hazardous. What makes MWFs different than most other lubricants, and potentially more hazardous to workers, is the way they are commonly delivered (as a mist or continuous spray) and the fact that workers are often in close proximity to the mist for an entire shift.

As primary agents of MWF deterioration, microbes have a tremendous impact on MWF system operations—from both health and economic perspectives. Microbial growth is associated with:

- Worker health issues
- Premature coolant disposal
- Waste disposal
- Workpiece defects
- Decreased tool life.

As microbes cause MWFs to break down, the fluids tend to lose their critical lubrication properties. Other byproducts of microbial activity include the build-up of noxious sulfur-like odors and increased foaming and misting of metalworking fluids, which facilitates worker inhalation and skin contact.

The obvious solutions would be to add biocides to MWFs and maintain high pH levels, which are hostile for bacteria. But while biocides do a good job of controlling microbial growth, many (most notably triazine, a formaldehyde releaser) create worker and environmental hazards. This is the primary reason why biocides must be registered with the EPA for each specific application.

On the other hand, some hazardous microbe species themselves cause worker illness. The two major microbe groups that have been recovered from MWFs are bacteria and fungi. Without biocides, water-based MWFs in particular would be breeding grounds for both of these organisms. The trick is finding a good way to control microbes without creating more problems.6

**MICROBES’ HEALTH EFFECTS**

Microbes proliferating in the absence of biocides can have health consequences. These microbes have the potential to cause three types of disease:

- **Infection.** The most common cause of infections among MWF workers is improperly treated wounds. It starts when minor skin puncturing injuries are caused by surfaces that carry bacteria and fungi. When the wounds are not cleaned and prop-

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**THE DIFFICULTY OF MEASURING MICROBES**

It’s often easy to smell and see microbe accumulation (especially on a Monday after MWFs have been inert for the weekend), but it’s not that easy to measure. And this is one of the difficulties in formulating biocides—quantifying the effect that they are having on bacterial and fungal colonies. There are three primary methods for quantifying microbes:

- **Microscopy**
- **Culture**
- **Chemistry.**

But no single test provides adequate information about the degree of bioburden, biological activity and the presence of microbes. One promising technique is quantitative real-time polymerase chain reaction (qPCR). This is a laboratory technique used to amplify and quantify DNA molecules. The PCR technique can be used to detect, identify and differentiate agents present in either clinical or environmental samples.

PCR is particularly useful in environmental microbiology because the population size of the organism can be determined and thus population changes can be tracked over time or in response to a change in the environment. The unquestionable success of detection assays based on PCR are largely due to its speed in comparison with many conventional diagnostic methods such as cultures.6

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Octopus arms can even react after they’ve been completely severed. In one
By buffer, pathogens multiply and cause infection. It’s important to note that there is no more risk of infectious disease in metalworking environments than anywhere else. It’s just that the risk of an injury (that could eventually lead to infection) is higher.

- **Toxemia.** This disease is caused by a poison. Microbial toxins include thousands of chemicals produced by bacteria and fungi. The three types of microbial toxins that could affect MWF workers are: endotoxins, exotoxins and mycotoxins (see Endotoxins, Exotoxins and Mycotoxins).

- **Allergies.** Unlike toxins, which would have a similar effect on nearly all exposed workers, allergens typically affect only a small percentage of workers who are sensitive to that particular allergen. An example of an allergen-induced condition is hypersensitivity pneumonitis.

**BIOCIDES**

STLE-member David W. Enright, Chemetall’s business manager for metalworking fluids, watercare, says, “There are benefits to using a biostable fluid. The elimination of sump side additions of strong biocides is an important improvement from a health and safety standpoint, as well as a significant cost saving from the biocide elimination. If formulated properly, there really isn’t a downside to the use of registered biocides or secondary amines such as dicyclohexylamine.”

Lou A. Honary, emeritus professor and director of UNI-NABL and currently president of Environmental Lubricants Manufacturing, Inc., defines a biostable fluid simply as, “a fluid that resists the growth of biological organisms.”

So is a bio-proof MWF even possible? Honary is skeptical. “It might be possible with reservoir built-in technologies that would kill bacteria on a continuous basis or create a hostile environment for bacteria,” he says. “Inline ozonators and newer technologies could be considered. Other technologies like air cooling and use of cooling gases could also be considered.”

**ENDOTOXINS, EXOTOXINS AND MYCOTOXINS**

*Endotoxins.* These are bacterial toxins consisting of lipids that remain within the cell. They are both toxic and allergenic—resulting in symptoms that range from mild fever to death from toxic shock.

*Exotoxins.* These are toxins secreted by bacteria. In contrast to endotoxins, they are highly potent and can cause major damage to the host. Examples include: E. coli and toxic shock-inducing S. aureus and S. pyogenes.

*Mycotoxins.* These are excreted exclusively by fungi. They are chemically diverse and capable of producing a range of conditions from hallucinations to cancer. Of the three toxins described here, they are the least likely to be found in MWFs.

**THE NEED FOR CONSENSUS DEFINITIONS**

There are some similarities between the terms fire-resistant fluids and biostable fluids. First of all, both terms once contained the word proof (fire-proof and bio-proof). But that word is rarely used in either context—with formulators opting for less imperative substitutes (resistant and stable). And there are currently no consensus definitions of either term. There is no authority that can definitively say what characterizes a fire-resistant fluid or a biostable fluid. To further complicate the situation, in the case of biostable fluids, the term biostable can refer to a fluid that is either rendered biostable by a biocide or a fluid where the microorganism population is under control for whatever reason.

This is how STLE-member David W. Enright, Chemetall’s business manager for metalworking fluids, watercare, characterizes a biostable MWF:

“A biostable fluid is one that resists the growth of bacteria and fungi when in use in a metalworking fluid operation. Optimally, the fluid achieves this stability without the use of registered biocides such as Kathon™ or the formaldehyde-releasing triazine types. As one can imagine, this is not easy, and several strategies have been employed including the use of the somewhat controversial dicyclohexylamine, which is among the compounds sometimes referred to as nonregistered biocides. Given this, the definition of a biostable fluid is one that is not subject to degradation by bacteria and/or fungus and achieves this property without the use of registered biocides or secondary amines such as dicyclohexylamine.”

Lou A. Honary, emeritus professor and director of UNI-NABL and currently president of Environmental Lubricants Manufacturing, Inc., defines a biostable fluid simply as, “a fluid that resists the growth of biological organisms.”

The EPA regulates biocides under the Pesticide Act of 1972 through the administration of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Under FIFRA, biocides require extensive toxicological testing since each biocide is registered for a particular application (see The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) on page 36). This registration process is similar to the federal FDA’s registration for pharmaceuticals and is more extensive than the notification requirements of the Toxic Substances Control Act (TSCA) for non-pesticide chemicals.
CLASSES OF BIOCIDES

Regulatory agencies are keeping a close eye on formaldehyde-releasing biocides, and they’ve been doing it for some time without taking drastic regulatory action—no agency has banned all formaldehyde-releasing biocides. However, formulators are seeing a trend in that direction. Some are taking a wait-and-see approach. Others, seeing the eventual ban of all formaldehyde-releasing biocides as an inevitability, are taking action to reduce or eliminate the formaldehyde-releasing MWF formulations that they offer.

FORMALDEHYDE RELEASERS

Formaldehyde-releasing biocides have been in use for decades for the same reasons that most other chemicals have been around a long time—they are both economical and effective against a spectrum of contaminants.

By far the most commonly used formaldehyde-releasing biocides are s-triazines (see Terminology). S-triazines are characterized by a symmetrical hexagonal ring with an alternating cycle of three carbon atoms and three nitrogen atoms. Carbon chains, which might or might not be oxygenated, are attached to the ring. S-triazine-based biocides are formed through a condensation reaction between equal amounts of alkanolamine and formaldehyde. The hydrolysis of formaldehyde at the cell wall effectively breaks down the microbe’s structure and leads to cellular death.

S-triazines are effective against a wide range of organisms even at the EPA-approved dose of 1,500 ppm.10 The health issue with s-triazines is formaldehyde. Although the short-term health effects of formaldehyde exposure are well known (watery eyes, coughing, etc.), less is known about potential long-term health effects.

In 1987 the EPA classified formaldehyde as a probable human carcinogen under conditions of unusually high or prolonged exposure. The International Agency for Research on Cancer (IARC) classifies formaldehyde as a human carcinogen, and in 2011 the National Tox-icology Program, an interagency collaborative of the Department of Health and Human Services, named formaldehyde as a known human carcinogen in its 12th Report on Carcinogens.

Since the 1980s, the National Cancer Institute (NCI) has conducted studies to determine whether there is an association between occupational exposure to formaldehyde and an increased cancer risk. The results of this research have provided the EPA and OSHA with information to evaluate the potential health effects of workplace exposure to formaldehyde.

A number of studies involving workers exposed to formaldehyde have recently been completed. One study, conducted by NCI, looked at 25,619 workers in industries with the potential for occupational formaldehyde exposure and estimated each worker’s exposure to the chemical while at work. The results showed an increased risk of death due to leukemia, particularly myeloid leukemia, among workers exposed to formaldehyde.12

There are approximately 30 s-triazines registered and approved by the EPA, but only two are registered and approved by the EPA as MWF antimicrobial agents. S-triazines as a class are currently under review by the EPA and have been since 2013. There is no target date set for completion and subsequent ruling. As mentioned earlier, the EPA has set an approved dose threshold that formulators find workable, but the need for cost-effective alternatives to s-triazines is evident.

THE FEDERAL INSECTICIDE, FUNGICIDE, AND RODENTICIDE ACT (FIFRA)11

When the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) was first passed in 1947, it established procedures for registering pesticides with the U.S. Department of Agriculture and established labeling provisions. The law was primarily concerned with the efficacy of pesticides and did not regulate pesticide use.

FIFRA was rewritten in 1972 when it was amended by the Federal Environmental Pesticide Control Act (FEPCA). The law has been amended many times. In its current form, FIFRA mandates that the EPA regulate the use and sale of pesticides to protect human health and preserve the environment. FIFRA provides the EPA with the authority to oversee the sale and use of pesticides, but it does not prevent local governments from regulating pesticide use. As FIFRA now stands, the EPA is authorized to:

1. Strengthen the registration process by shifting the burden of proof to the chemical manufacturer
2. Enforce compliance against banned and unregistered products
3. Promulgate the regulatory framework missing from the original law.

TERMINOLOGY

• Metalworking fluids (MWFs) are also calling cutting fluids, cooling fluids and coolants.
• Biocides also are referred to as pesticides—primarily because the EPA treats them the same.
• S-triazine also is called 1,3,5-triazine or cyanuric chloride, but is commonly referred to simply as triazine.
• Microbes also are called microorganisms and are sometimes referred to as bacteria, viruses or germs.
• Formaldehyde also is called formalin, methanol, methyl aldehyde, methylene oxide, morbicid acid and oxymethylene.
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FORMALDEHYDE-FREE ALTERNATIVES

Many formulators are frustrated at the need to formulate-out formaldehyde-releasing biocides due to regulations and consumer demand. But there are approved alternatives (see Figure 1). For example, Europe’s BPD (Biocidal Products Directive) lists 30 approved biocides for MWFs. Of these, only 10 are formaldehyde-releasers.

One of the most widely used formaldehyde-free biocides is benzisothiazolinone (BIT). BIT is very stable and is able to preserve a fluid for a long time. However, BIT has effectiveness issues, notably against pseudomonas and fungi, which are commonly found in contaminated MWFs. The solution is to combine BIT with another biocide such as nitromorpholine, which fills in BIT’s efficacy gaps. An added bonus is that nitromorpholine does not release formaldehyde under the conditions found in most MWF formulations.

Sodium ortho-phenylphenate (NaOPP) and ortho-phenylphenol (OPP) are two more alternatives. They are highly effective, broad-spectrum biocides—although not without toxicity issues of their own.

Two additional formaldehyde-free chemistries are methyl isothiazolinone (MIT) and glutaraldehyde. MIT is a good bactericide and effective at controlling mycobacteria (see What are Mycobacteria?). However, it can be difficult to stabilize in an MWF formulation. Since glutaraldehyde can cross-link amines, it is best for formulations that do not contain amines.

In November 2001 the Centers for Disease Control (CDC) reviewed a case involving three machinists from an automobile brake manufacturing facility in Ohio that were hospitalized for respiratory illness. A review of the facility’s personnel records found that 107 (27%) of the 400 workers had been placed on work restriction by their physicians during the preceding 11 months due to respiratory conditions. Multiple samples of MWFs from all central plant systems were analyzed. This testing revealed a newly proposed species—Mycobacterium immunogenum or M. immunogenum.

Mycobacteria are unicellular, aerobic, weakly gram-positive but still acid-fast bacteria. They are broadly grouped into two major categories based on pathogenicity for animals and humans. The extremely pathogenic organisms M. tuberculosis and M. leprae must transfer directly from host-to-host without exposure to the environment, but the majority of the species, such as M. smegmatis, M. terrae and M. immunogenum, are ubiquitous in the environment. M. immunogenum has been implicated as a cause of the lung condition hypersensitivity pneumonitis, which has been linked to chronic exposure to MWF mists. The metalworking industry has been working overtime to control mycobacteria and eliminate MWFs as a source of hypersensitivity pneumonitis.

Interestingly, triazine-based biocides, while effective against a host of microbes, do not control M. immunogenum well—some researchers have speculated that triazine actually encourages the growth of M. immunogenum.

Figure 1 | Alternatives to formaldehyde releasers.

<table>
<thead>
<tr>
<th>Biocide</th>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIT (benzisothiazolinone)</td>
<td>• Very stable&lt;br&gt;• Excellent compatibility</td>
<td>• Possible efficacy gap</td>
</tr>
<tr>
<td>Dinitro-morpholines</td>
<td>• Effective against fungus&lt;br&gt;• Good stability&lt;br&gt;• Lower use rate&lt;br&gt;• Easy to formulate</td>
<td>• Odor issues&lt;br&gt;• Nitrosamine concerns (possible carcinogens)&lt;br&gt;• Low water solubility</td>
</tr>
<tr>
<td>MIT (methyl isothiazolinone)</td>
<td>• Effective against fungus</td>
<td>• Variable stability&lt;br&gt;• Stabilizer costs</td>
</tr>
<tr>
<td>Phenolics</td>
<td>• Effective against fungus&lt;br&gt;• Very stable</td>
<td>• Odor issues&lt;br&gt;• Discharge restrictions&lt;br&gt;• Cost</td>
</tr>
<tr>
<td>BIT + Nitro-dimorpholine</td>
<td>• Easy to formulate in concentrates&lt;br&gt;• Good stability&lt;br&gt;• Good bacterial/fungal spectrum&lt;br&gt;• Effective against fungus&lt;br&gt;• Less odor than nitro-dimorpholine alone</td>
<td>• Potential odors/sensitization&lt;br&gt;• Nitrosamine concerns (possible carcinogens)</td>
</tr>
</tbody>
</table>

Source: Dow Microbial Control
Applications, Additives, and Tailored Customer Service

PCC Chemax has new opportunities and levels of potential to offer. We always work with our customers to tailor products and services to meet your needs.

Our knowledgeable, informed, and skilled technical experts help you create customized, tailored, and measurable solutions.

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- Metal Plating
- Polymer Additives
- Textile
- Construction
- Corrosion Protection
- HI&I
- Oilfield
Other formaldehyde-free biocides include dibromonitrilopropanionamide (DBNPA) and bromo nitropropanediol (Bronopol), but since they both degrade quickly in MWFs they are better for tank-side fluid.15

A final intriguing alternative is methylenebismorpholine (MBM). This is an EPA-registered chemical. Although technically a formaldehyde releaser, the amount of formaldehyde is negligible when compared with other formaldehyde releasers—about 1.1 parts per billion with an estimated maximum concentration of 3.3 ppb. That’s well below the EPAs occupational level of concern of 100 ppb.

“Of course, the market embraces fluids that achieve biostability without biocides,” Enright says. “The elimination of the need for formaldehyde releasing materials such as triazine has been welcomed in the marketplace especially since the declaration by the National Toxicology Program that formaldehyde is a known human carcinogen. The elimination, or at least the drastic reduction, in the need for the use of the very strong isothiazoline (Kathon™)16 type biocides provides significant health and safety risk reduction and cost savings.”

**REDUCING BIOLOGIC MATERIAL WITHOUT BIOCIDES**

The best way to control microbes without biocides is to avoid creating a friendly habitat for microbes in the first place. This includes keeping the coolant and the sump as clean and free from impurities as possible. Another method is to choose MWFs with biostatic properties. These are coolants that are not affected or consumed by bacteria. However some coolants that are labeled biostatic still require biocides, so they are not truly biostatic.

“In general, a price premium of up to 10% is not uncommon as the bioresistant raw materials needed to formulate a biostable fluid are more specialized and proprietary,” Enright explains. “This initial premium is easily recovered by the savings realized by not having to use registered biocides and the reduction in the amount of metalworking fluid used over time as a result of better bioresistance. Of course, there are savings realized from the safety, health and environmental standpoint as well. Harder to quantify, but definitely real, are cost savings gained from the reduction or elimination of worker and environmental exposure to these harsh chemicals.”

Pasteurizing MWFs will kill bacteria, as well adjusting the pH. Other nonchemical alternatives to biocides include ultraviolet irradiation and membrane filtration. Membrane filtration with an embedded sensor, in particular, is an intriguing process since it can detect microorganisms when they begin to form.

Lou A. Honary, emeritus professor and director of UNI-NABL Center and currently president of Environmental Lubricants Manufacturing, Inc., says, “We are working on more stable bio-based MWFs that require less biocide and work in a variety of water types. The biobased MWFs present a new frontier for MWFs and simultaneously a new set of challenges.”

**HOUSEKEEPING PRACTICES**

The coolant should be filtered and recycled regularly. The machines also should be broken down and cleaned at least once each year. A regular and systematic cleaning of the sump and coolant also should be completed. Coolant management—which could reduce the need for biocides—starts with continuously removing metal chips and tramp oil and then thoroughly cleaning the system on a regular basis as follows:

1. Pump coolant from the sump.
2. Remove all remaining metal chips and fines.
3. Remove oily residues from all surfaces.
4. Fill the sump with a good cleaner using clean water.
5. Circulate the cleaner through the coolant system for several hours.
6. Apply cleaning solution to machine surfaces that are not contacted by the coolant during machine operation.
7. Pump cleaning solution from the sump.
8. Wipe cleaning solution residues from the sump.
9. Rinse the entire coolant system with clean water.
10. Recharge the system with reclaimed or new coolant immediately to protect metal surfaces against corrosion.17

While formaldehyde-releasing biocides have been around for a long time, ever more stringent regulatory pressures have been forcing formulators to investigate alternative chemistries. Formulators have to walk a line between effectiveness and cost.

The solutions for the problem of DDT were developing effective substitutes and learning how to control the mosquito population through natural means. That’s about where MWF biocides are headed—substitution with less toxic formulations coupled with more attention to workplace hygiene.

STLE-member Dr. Dave Slinkman, senior vice president, Global Research and Technology, Houghton International, Inc., explains, “From a benefits perspective, biostable fluids extend sump life; eliminate odors, which results in increased operator acceptance; minimize waste treatment, disposal and fluid recharge costs; and minimize or eliminate the need for sump-side additives.

“All of these benefits are provided in addition to providing all the needed performance features, including but not limited to lubricity, cooling, corrosion protection, machining performance, cleanliness and flushing of metal chips. We don’t see any drawbacks of using biostable fluids.”

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