Metalworking fluids: The quest for bioresistance

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KEY CONCEPTS

Microbial contamination can lead to premature failure of MWFs and health and safety issues.

MWF formulators have a number of options in developing products that can resist microbial contamination.

With the decline in the number of available biocides, MWF formulators will use combinations of biocides and non-biocidal additives to prepare fluids that resist microbial degradation.

By Dr. Neil Canter
Contributing Editor

The main objective in working with metalworking fluids (MWFs) is to extend their operating life as long as possible. Microbial contamination remains one of the key reasons why MWFs fail prematurely.

MWF formulations are complex because they contain a large number of organic components needed to fulfill specific functions. These components may be food for microbes such as bacteria and fungi that can exist in these systems operating at ambient temperature in an open environment. Degradation of MWFs not only leads to premature failure but also can cause health and safety concerns to workers maintaining them.

The main components used in a MWF to control microbial contamination are biocides. There have been many types available in the marketplace that have demonstrated varying degrees of effectiveness. The MWF industry has been able to work with them successfully.

But regulations such as the European Union's (EU) Biocidal Products Regulation (BPR) and concerns about working with formaldehyde-condensate biocides are reducing the number of options available to the MWF industry. Other concerns are surfacing such as raw material availability, which led to a shortage of the widely used biocide benzisothiazolinone (BIT) in the 2018 marketplace.[1]

With the MWF industry facing declining options, formulators are looking for other approaches to develop bioresistant MWFs. The purpose of this article is to discuss the challenges faced by MWF suppliers in developing products that exhibit high levels of bioresistance.

Input on the issue was obtained from industry experts who have perspectives from the biocide, additive, independent consultant and formulator standpoints.

The following individuals were contacted.

1. Nicole Clarkson, ANGUS Chemical Co.
2. Dr. Fred Passman, BCA Inc.
3. Robert Ash, Eastman Chemical Co.
4. Uwe Falk, The Lubrizol Corp.
5. Michael Kosalko, Quaker Chemical
6. Stefan Sakulowski, Schülke & Mayr GmbH
7. Rex Curtis, Troy Corp.
8. Dr. Helen Ngo and Karen Wagner, USDA
9. Jerry Byers, independent consultant
10. Dr. Alan Eachus, independent consultant
11. Anonymous industry representative.

Microbes and MWF failure

STLE Fellow Dr. Fred Passman, principal for BCA Inc. in Princeton, N.J., says, "Microbes are implicated in several MWF failure mechanisms shown below."

- Weak acid metabolites can react with chloride and other salts to form weak organic bases and strong inorganic acids (hydrochloric being the most prevalent).
- Microbes use various MWF components as food, thereby selectively depleting MWF of functional additives and degrading MWF performance.
- Historically odor was the primary reason for draining MWF systems. Many microbial metabolites are volatile organic compounds (VOCs) that create an aroma that is similar to that of a swamp.

Passman continues, "The primary health risk posed by MWF microbes is allergenic diseases ranging from mild allergic rhinitis to potentially fatal hypersensitivity pneumonitis (HP). Given that for most allergens, only a small percentage of the exposed population is sensitive, it is difficult to predict how or whether a given antigen will affect workers."

STLE-member Uwe Falk, global commercial manager biocides for The Lubrizol Corp. in Hamburg, Germany, indicates that most components present in typical MWFs are susceptible to microbial attack, especially if those components are easily biodegradable. He says, "While substances being attacked by microbes will not only lose their functions, the formed degradation products may have an additional negative impact on stability and performance (formation of acids, etc.). Unfortunately various factors can lead to poorer worker health and safety, such as excess microbial growth, insufficient mist controls, improper personal protective equipment, etc."

Minimization of these MWF related problems can be done by following best practices that are found in documents published by OSHA and the UKLA.[2,3]

Besides generating acidic metabolites, STLE Life Member Dr. Alan Eachus, an Illinois-based independent consultant who holds STLE's CMFS certification, lists several other ways microbes can cause MWF failure.

Says Eachus: "Microbes can produce biofilms leading to slime production that cause filter blocking and impede fluid flow. They can selectively deplete fluid components causing emulsions to split, loss of corrosion inhibition and increased foam. Microbes also can generate unpleasant odors and bioaerosols in mists that can negatively impact workers' productivity and health."

STLE-member Rex Curtis, business manager global MWF Unit for Troy Corp. in Florham Park, N.J., and colleagues discuss the mechanism for how microbes break down components in the MWF. Curtis says, "Typically, fluid components are attacked oxidatively. This is a gradual process in which unsaturated bonds become saturated, side chains are removed from complex molecules, and chain lengths are reduced. The byproducts of attack by one type of microorganism may in fact become the food source for another. Components present in a MWF are not all equally degradable, and some will be attacked at a more rapid rate than others."

Two specific health effects from microbes that can affect exposed workers are bacterial endotoxins and HP. Curtis says, "Endotoxins are lipopolysaccharides that are found in the outer membrane of the cell wall of Gram-negative bacteria. The health effects of endotoxins in MWF operators have been well documented. Inhalation can cause an inflammatory response in the lungs that includes acute (fever, respiratory symptoms, etc.) and chronic (chronic productive cough due to bronchitis and accelerated lung function decline) effects."

Curtis continues, "HP was first reported in the U.S. in 1992, and numerous reported cases have occurred in both the EU and the U.S. It can include both acute, sub-acute and chronic illnesses that can include fever, cough, progressively worsening breathlessness as well as weight loss."

STLE-member Robert Ash, product director for Eastman's Care Chemical business, identifies specific compounds produced by microbes that are the source of noxious odors. He says, "Bacteria/fungi produce methanediol (usually from the amino acid methionine) and hydrogen sulfide, which both yield a sulfurous fecal smell. Some microbes produce shorter chain carboxylic acids (e.g., valeric acid) that have a smelly feet sort of odor."

Past President and STLE Fellow Jerry Byers, a Florida-based independent consultant and editor of the book Metalworking Fluids, Third Edition, points out that fungal growth can clog MWF supply lines. He says, "Additionally, a number of studies have shown a link between certain microbial organisms in MWF and respiratory issues. However, dermatological studies have proven that microbial species do not cause skin irritation."

Stefan Sakulowski, product development manager personal care/industrial biocides for Schülke & Mayr GmbH in Norderstedt, Germany, indicates that decomposition of the components in the MWF also can impact performance. He says, "With the decomposition of additives, the quality of the workpiece undergoing specific machining operations also is negatively affected."

STLE-member Nicole Clarkson, global metalworking fluid segment leader for ANGUS Chemical Co. in Buffalo Grove, Ill., says, "Microbes utilize certain components in MWFs as a food source such as carbon, sulfur, magnesium, oxygen, etc. These components are essential to the overall performance of the fluid, and once utilized key MWF functionality is often lost."

An industrial representative who prefers anonymity states that the presence of microbes can be more of a problem for the stability of the fluid than for healthy workers in close proximity to the MWF system. This individual says, "Microbes can cause rapid infection of cuts that come in contact with the fluid. In some cases, the specific microbes in the fluid can pose a risk to worker health and safety, most often through accidental inhalation of mist or exposure through skin abrasions. Sometimes the membranes of dead organisms can cause irritation if accidentally inhaled."

Definitions

In making claims about the ability of MWFs to withstand microbial contamination, the terms bioresistant, biostatic and biostable are used. The contributors to this article were asked for their definitions and if there is any distinction among the three terms.

Byers points to ASTM E2523 (Standard Terminology for Metalworking Fluids and Operations) for definitions of bioresistant, biostatic and biostable.[4] He says, "This ASTM standard considers bioresistant to be fluids that have the ability to withstand microbial attack. Biostatic MWFs are able to prevent existing contaminating microbes from growing or proliferating but are unable to kill them. MWFs resistant to the effects of microorganisms and remain chemically stable are bioresistant."

Byers continues, "Based on these definitions, it appears that bioresistant and biostable refer to being stable despite the presence of microbes, while biostatic means keeping microbes from multiplying without killing them. However, the terms tend to be used interchangeably."

Curtis says, "The distinction among the terms are blurred, and different people will have different interpretations. MWF formulators design MWF products to accomplish a number of different but all-important objectives for the end-user. At the onset of the process, some formulators utilize raw materials, including biocides, with the intent to prevent bacteria and fungi from growing. Some would say that this type of formulation strategy creates a bioresistant product. We define bioresistant products as products where detection of significant levels of viable organisms in freshly prepared in-use fluids is limited, as they are actively being killed by the antimicrobials present in the working solution."

Curtis continues, "Another way to stave off growth is through using raw materials that are weaker food sources for microbes. In these formulations, organisms may be present and easy to detect in the in-use fluid, but the absence of food prevents microbes from rapidly growing. These would be considered biostable MWFs."

Curtis continues, "The term biostatic, although not uncommonly used in Europe for MWFs, is generally not seen in North America, likely based on concerns that it would be interpreted as a claim that the MWF product is a biocide and is subject in the U.S. to FIFRA and requires EPA registration."

Ash says, "The terms bioresistant, biostatic and biostable do not, to our knowledge, have accepted standard definitions. Our suggested definitions are listed below, and please note that there is some overlap."

- **Bioresistant.** MWFs containing a number of components that are not biocides and are known to slow or stop the growth of microbes (sometimes specific ones and sometimes all microbes). Bioresistant fluids also may contain biocides, but the designation bioresistant is meant to imply that non-biocidal components are resistant to microbes. For example, a fluid containing an N-alkyl-alkanolamine that prevents microbial growth would be bioresistant.
- **Biostatic.** A MWF in which microbial inoculation will not grow and by implication will die. Biostatic can be taken as the superlative of bioresistant. The terms bioresistant and biostatic are often used interchangeably.
- **Biostable.** A MWF that is sufficiently stable against microbial growth within the fluids typical work environment.

Sakulowski believes that there is difficulty in differentiating among the three terms. He says, "In the EU market, the three terms are used more or less identically to describe MWFs that do not contain conventional biocides. Bioresistant and biostable are comparable in my opinion and both terms describe a MWF that is resistant/stable against microbial growth. The term 'static' describes a fluid that can become contaminated with microbes, but they will not be able to grow/increase."

The industrial representative considers bioresistant fluids to be unable to support microbial life. This individual says, "Given several inoculations with microbial organisms (both bacterial and fungal) these fluids are unable to show signs of contamination. Biostatic fluids are able to support some limited microbial life, either by not killing spores or by restricting the growth but not outright killing the organisms."

Michael Kosalko, North American lab manager, metalworking for Quaker ▶▶▶

Chemical in Conshohocken, Pa., feels there is a lot of crossover between the definitions of bioresistant and biostatic from person to person. He says, "Both imply a specific design to inhibit microbiological growth. Biostable, on the other hand, implies that the MWF chemistry is stable in the presence of microbiological organisms."

Eachus says, "The distinctions among the terms bioresistant, biostatic and biostable are subtle at best; the words are often used interchangeably. A bioresistant fluid would be expected to not permit the proliferation of microbes within it, while biostatic or biostable fluids would be expected to remain unchanged despite an increase in microbial load."

Passman believes there is no difference between bioresistant and biostatic but both terms are distinct from biostable. He says, "A *bioresistant or biostatic* MWF tends to inhibit microbe proliferation. If left to stand or if exposed to repeated challenges, and end-use dilutions, bioresistant/biostatic MWF population densities will remain less than 1E4 CFU (Colony forming unit) per ml and less than 1E3 CFU per ml, bacteria and fungi, respectively."

Passman continues, "Biostable MWFs can tolerate greater than 1E6 CFU/ml bioburdens without showing evidence of biodeterioration (i.e., pH and reserve alkalinity remain constant as do concentrations of formulation components)."

Available biocides

The managers were asked to review the current biocides still available for use in MWFs. Falk says, "Formaldehyde condensates are still a valuable option, as most of them are still seen as safe technology. In fact, aldehydes such as formaldehyde condensates are the only types of biocide known to be able to control endotoxins. While the class of isothiazolinones is under increasing pressure for its sensitizing potential and labeling, they should maintain a strong position through synergistic biocide combinations. Phenol derivatives may see a revival, while they may not become more than niche players. Classical fungicides such as iodopropynyl butyl carbamate (IPBC) and sodium pyrithione may synergistically boost the performance of classical biocides. Even special amines authorized as biocides may work, though there may be challenges to add these to already-formulated MWF concentrates."

Sakulowski says, "Formaldehyde condensates are still widely used. They have low use concentrations (0.1%-0.2% in the final emulsion) and can be formulated into the MWF concentrate. Chloromethylisothiazolinone/methylisothiazolinone (CMIT/MIT) also is an option, but the stability of this blend of biocide actives in the MWF is not that good, and high sensitization potential also is a big risk regarding worker health and safety."

Microbial contamination remains one of the key reasons why MWFs fail prematurely.

Curtis says, "The two primary categories of bactericides used either tankside or in MWF concentrates are formaldehyde condensates (triazine and non-triazine alternatives) and isothiazolinones (BIT/CIT/MIT). Despite the growth of BIT and non-triazine alternatives, hexahydrotriazine (HHT) remains by far the largest volume bactericide used in MWF concentrates in North America. Phenolics, although registered for use in MWFs, continue to be constrained by concerns over waste water discharge regulations. Cationic polymeric bactericides are used in synthetic MWFs."

Curtis continues, "The most commonly used fungicides in MWF concentrates continue to be IPBC, sodium pyrithione and butylbenzisothiazolinone (BBIT)."

Passman considers formaldehyde condensates and isothiazolinones to be the workhorse biocides used in MWFs. He says, "Although the relationship is only marginally casual, as the variety of formaldehyde condensates decreased, the number of isothiazolinone chemistries have increased. Most isothiazolinone actives have one or more high volume addressable markets to justify new active ingredient development and biocide/pesticide registration. The MWF sector is simply an orphan add-on."

Passman continues, "Conversely as formaldehyde continues to experience regulatory pressure, the economic justification for developing and registering new actives of this type is simply not there. Currently, there are 47 active biocide ingredients approved by the EPA for use in MWF and 27 with dossiers under the BPR."

The industrial representative is in agreement with the currently available biocide options in MWF concentrates. This individual indicates that more options are available for tankside biocides and says, "Isothiazolone chemistry [CMIT/MIT, dichlorooctylisothiazolone (DCOIT) and octylisothiazoline (OIT)] can be used tankside along with dibrononitrilopropionamide (DBNPA), which is a fast-acting biocide that can knock down microbial populations quickly."

Eachus cites the building regulatory pressure, often starting in Europe, on the widely used biocide classes of formaldehyde condensates and isothiazolinones. He says, "Further information can be found in a blog[5] associated with Wallenius Water, a Swedish company."

Eachus continues, "As a result of the regulatory pressure, non-halogenated phenolics, IPBC, DBNPA and bronopol should assume more prominence as MWF biocides while other options such as pyrithiones, dimethyldithiocarbamates, glutaraldehyde and nitrobutylmorpholine also may be increasingly used. Caution should be used as all biocides exhibit positive and negative characteristics."

Eachus concludes, "Combinations of these active antimicrobials also will be used more frequently."

HHT

Concern continues to exist about whether the widely used biocide HHT can still be used at its recommended MWF end-use concentration of 1,500 ppm. The contributors were asked about the status of HHT and whether formulators should still continue to use it.

Passman says, "EPA's Office of Pesticide Programs (OPP) has yet to issue its final Re-Registration Eligibility Decision (RED) on HHT manufactured by one of the several companies who produce the biocide. This makes the curious phenomenon of having dif-

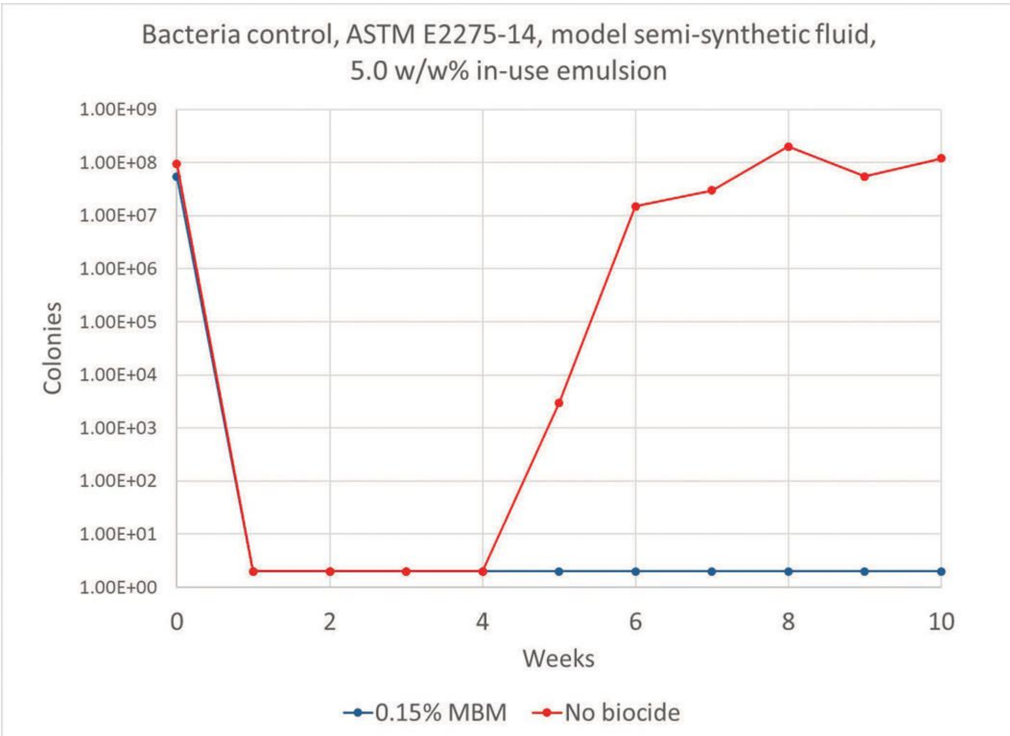

Figure 1. **In a study using ASTM E2275-14, two semisynthetic fluids were evaluated for bioresistance. The fluid formulated with a biocide (blue curve) displayed superior performance after being tested for 10 weeks compared to the identical fluid without a biocide (red curve).** *(Figure courtesy of The Lubrizol Corp.)*

ferent maximum permissible treat-rates, depending on the source of HHT. Consequently, HHT can still be used at effective concentrations. HHT has a greater than 50-year history of effective use in a broad range of MWFs. HHT's toxicological profile does not resemble that of formaldehyde.[6] Moreover, C^{13} NMR data showing that free-formaldehyde is undetectable in triazine solutions at MWF pH (i.e., >8). If the MWF industry can overcome the anti-formaldehyde hysteria, then formulators should definitely continue to use HHT."

Eachus says, "HHT is the formaldehyde-condensate whipping boy being accused of creating carcinogenic levels of free formaldehyde in MWFs. European regulators are designating it as a candidate for substitution. HHT is not totally banned everywhere, but its maximum permitted level, under various regulatory scenarios, is expected to be restricted to concentrations well below any antibacterially effective amount. A similar fate is potentially faced by other formaldehyde-condensates, but MWF formulators should continue to work with them because they can work quite well in combinations with other, non-formaldehyde-based biocides."

Curtis indicates that HHT is being supported in the current EPA Registration review process and continues to be widely used due to excellent cost performance. He says, "Use of formaldehyde-based biocides such as HHT should continue because these are the ones that are effective at neutralizing endotoxins in MWFs. Past studies by Douglas and Rossmoore[7] demonstrate the effectiveness of formaldehyde condensates. Non-formaldehyde alternatives such as isothiazolinones do not have this additional benefit."

The industrial representative cautions that each MWF formulator should assess its current product line due to the high degree of uncertainty in the timing around any potential regulatory decisions concerning HHT. This representative says, "If a formulator's product line relies heavily on HHT, it might be a good time to consider a few new formulations with other biocides. The important thing is to be aware of the potential for changes to use levels of HHT in the future and have a plan in place in case there is a change."

Falk says, "HHT is still a viable option for various applications. Where concerns exist, other formaldehyde condensates are available in the marketplace, such as methylenebismorpholine (MBM), which releases a far lower amount of formaldehyde than HHT during typical use in MWFs."

Figure 1 shows a study done using ASTM E2275-14 (Standard Practice for Evaluating Water-Miscible Metalworking Fluid Bioresistance and Antimicrobial Pesticide Performance) that involved a semisynthetic fluid formulated with less bioavailable ingredients. One study was done with the formulation without biocide (red curve) while a second formulation contained the identical components plus 0.15% MBM (blue curve). Both fluids were diluted to 5% prior to testing.

Falk says, "In the initial four weeks of the study, no microbial growth was seen in either fluid. But microbial growth increased dramatically during week #5 and week #6 for the formulation without biocide because the microbes adapted to the MWF system. In contrast, no microbial growth was detected in the formulation with MBM for the duration of the test (10 weeks)."

Sakulowski indicates that in the EU, the first three formaldehyde condenates have been reclassified with the H350 (may cause cancer) hazard statement based on the theoretically splittable content of formaldehyde. He says, "We expect all formaldehyde condensates including HHT to be classified identically in the upcoming years, and it will impact the MWF concentrate. It is important to note that the use of these formaldehyde condensates in the MWF during use is safe, and there is no need for the H350 hazard statement. A similar situation exists in the U.S. where HHT is classified as toxic in a MWF concentrate but safe in the MWF during use."

BIT

When asked about the BIT supply situation, most of the respondents indicated that it will be temporary, and pricing for BIT and other isothiazolinones will increase. Curtis says, "The BIT supply situation continues to be monitored very closely. While supplies of BIT are not yet back to normal, it is expected that this will be the case by the second half of calendar year 2019. In the interim, this situation continues to put pressure on biocide suppliers and ultimately MWF formulators. Yes—BIT will continue to be a viable, non-formaldehyde alternative that is an effective biocide used in both MWF concentrates and tankside applications."

Eachus says, "Currently the manufacture of the precursor intermediate (ortho-nitrochlorobenzene) for production of BIT is under pressure from the Chinese government for environmental reasons, and BIT manufacturers have been notified of its scarcity. BIT is very widely used in a number of markets, including MWFs. Despite its known skin sensitizing properties, it remains approved in cosmetic applications in Europe. It is inconceivable that non-Chinese suppliers would not recognize this opportunity and fill the gap. This may take a while, causing short-term disruptions, but BIT is a less unattractive member of the isothiazolinone family with regard to regulatory pressure, than are CMIT and MIT, and may be expected to remain available as a MWF preservative for some time."

Sakulowski says, "BIT will still be used as a biocide in MWF applications in the future but more likely in combination with other biocide actives as the efficacy of BIT alone may not be sufficient."

Passman feels that the current BIT supply shortage reflects the increasing disconnect between management at biocide manufacturers and the technical realities of the MWF industry. He says, "It was simply illogical for the original manufacturer of BIT to cease production of the reactive intermediate (ortho-nitrochlorobenzene) and even less logical for all BIT producers to rely on a single producer of this intermediate. While raw material cost considerations are important, supply reliability is equally important."

Passman continues, "BIT is effective in some MWFs but not in nearly as many as formaldehyde condensates. Most biocide manufacturers sell BIT as an active in a formulated product that includes one or more additional biocides. BIT certainly has a place in the portfolio of MWF biocides, but the current availability crisis has made MWF formulators wary."

Phenolics

Phenolic biocides can be effective in MWFs but do have positive and negative issues that formulators must deal with when used. Byers says, "Phenolics can be effective but suffer from three issues: odor, difficulty to remove in waste treatment and certain phenolics contain chlorine that many end-users will not accept."

Passman says, "The two major negatives against phenolic biocide use in MWFs are cost and potential for colorimetric tests to detect phenolics in metalworking facility wastewater. Phenolics cost three to five times as much as the alternatives on a cost-to-treat 1,000 gallons of MWF. The issue is due to a combination of the high concentrations needed (typically 2,000-5,000 ppm in end-use diluted MWF) and product cost per pound."

Passman continues, "Formulating with phenolics can be a challenge because one active, ortho-phenylphenol (OPP) is available as a water-soluble sodium salt and the other phenolic products are oil-soluble. Given their oil/lipid solubility, phenolics are generally more effective than other biocide actives against acid fast bacteria such a *Mycobacterium immunogenum* (one of the species known to cause HP)."

Eachus says, "Phenolic compounds have been established as biocides for a long time, in a number of applications. They are neither formaldehyde condensates nor isothiazolinones, are relatively chemically stable, exhibit broad-spectrum efficacy and are not consumed in the course of their antimicrobial activity. Besides their negative impact on municipal sewage, which is most prevalent with halogenated derivatives, another perceived negative of phenolics in general is their characteristic odor."

Boric acid

Eachus says, "Boric acid and its amine salts are well-established pH buffers and corrosion inhibitors in MWFs and are known to confer enhanced bioresistance to these fluids. Due to its non-toxic nature, boric acid is used in ocular medications and other sensitive applications. EU regulators have seen fit to declare boric acid as a reproductive toxin, Category 1B. While concentrations of boric acid requiring a label of 'Danger' are higher than those which would be expected to be encountered in MWF concentrates, many end-users are nevertheless demanding boron-free MWFs. This removes a valuable contributor to the inherent bioresistance of MWFs. A recognized technical shortcoming of boron chemistry in MWFs, though, is the tendency for certain boric acid-amine salts to form difficult-to-remove residual deposits on substrates from dried fluids."

Byers says, "Boron-based chemistries are quite popular among formulators. While not perfect, boron does help with microbial control and borates are excellent rust inhibitors—truly multifunctional raw materials! However, borates can lead to residue problems, and free boric acid content over 5.5% means the MWF would require a Health Hazard GHS pictogram and 'Danger' signal words, so efforts should be made to ensure free boric acid is below this level."

Falk says, "We have observed that more companies are switching to boron-free fluids or claiming that they plan to switch in the future."

Specialty amines

Ash and Clarkson both indicate that a number of specialty amines can extend or expand the utility of registered biocides, including butylaminoethanol and 3-amino-4-octanol.

Clarkson adds, "Chemistries such as monoethanolamine (MEA), aminomethyl propanol (AMP), monoisopropanolamine (MIPA) and diglycolamine (DGA) also help improve fluid longevity, as they can impart a variety of performance attributes in a MWF formulation but to a lesser extent. The exact mode of action of specialty amines will likely change from one amine/biocide combination to the next."

Ash considers the mechanism for how specialty amines work to minimize microbial contamination to be interesting. He says, "Some early theories involved migration of uncharged amines from the basic extracellular fluid into the lower pH intracellular fluid whereupon protonation would alter the osmotic pressure and rupture the cell. Later theories focused on membrane synthesis and lipid incorporation into membranes. We do not consider the issue to be settled at this point."

Clarkson says, "The exact mode of action of specialty amines has not been fully evaluated and will likely change from one amine/biocide combination to the next."

To demonstrate the effectiveness of specialty amines with the biocide BIT, five variations of the semisynthetic fluid containing the components shown in Table 1 were prepared with the five amines listed in Figure 2. Each of these amines only demonstrated microbial control for three weeks. When specialty amines of the types shown in Figure 3 are added to each of or a combination of the amines shown in Figure 2, microbial control improved dramatically in specific cases.

Table 1. **Components used in formulating semisynthetic fluids with the amines listed in Figure 2 and Figure 3.**

Components Formulated into a Semisynthetic Fluid With Amines
Naphthenic Oil
Sodium Petroleum Sulfonate
Tall Oil Fatty Acid
Phosphate Ester
Propylene Glycol N-Butyl Ether
Co-Emulsifier (as needed)
Acid/Amine
BIT (20% Active)

(Table courtesy of ANGUS Chemical Co.)

Eachus says, "A recent study showed that combinations of various specialty primary alkanolamines enhanced the efficacy of a number of MWF biocides.[8] Dicyclohexylamine (DCHA) also boosted biocide efficacy in this study and has been used for some years by the MWF industry in this regard, but there are concerns over its potential for dermal toxicity, and it is not universally accepted."

Passman says, "It has been demonstrated that more complex amines are more bioresistant than simpler amines. Complex amines that have been tested to show they have specific, non-biocidal performance properties, and—based on ASTM E2275 or similar MWF speed of kill testing—have no biocidal performance, show great promise as biostable MWF functional additives. Amines that function primarily as biocides should be used only if they have the requisite biocide registrations."

Other biocide options

Despite the trend for fewer options, at least one new biocide has been introduced recently. Sakulowski says, "A biocide based on a blend of phenoxyethanol, BDA (laurylamine dipropylenediamine) and BBIT was commercialized in 2017. This product is typically added tankside to the MWF at a relatively high concentration (0.3%-1.0%) but also is stable in a MWF concentrate."

Sakulowski continues by explaining how the three biocide actives complement each other. He says, "The BDA acts as a quick killer to any possible contamination already existing in the MWF in a few minutes. This eliminates the first source of microbiological growth. Phenoxyethanol is more active in controlling bacterial growth and BBIT is a pure fungicide. All three actives complement each other in a patented synergism that leads to a much lower use concentration compared to the use of the actives individually."

Sakulowski indicated that this new biocide is available in most regions globally except for the U.S. at this time.

A new type of biocide under development contains a poly-phenolic branched-chain fatty acid structure *(see Figure 4)*. Karen Wagner, technical scientist for the USDA in Wyndmoor, Pa., says, "Poly-phenolic branched-chain fatty acids have

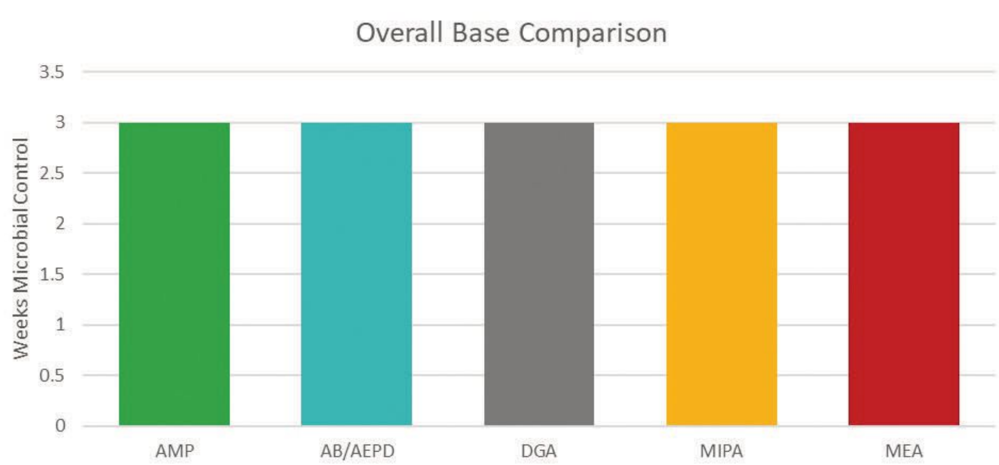

Figure 2. **The five amines shown (AMP: aminomethyl propanol, AB/AEPD: aminobutanol/ 2-amino-2-ethyl-1,3-propanediol, DGA: diglycolamine, MIPA: monoisopropanolamine and MEA: monoethanolamine) were each formulated into a semisynthetic fluid containing the components listed in Table 1. Each formulation only showed microbial control for three weeks.** *(Figure courtesy of ANGUS Chemical Co.)*

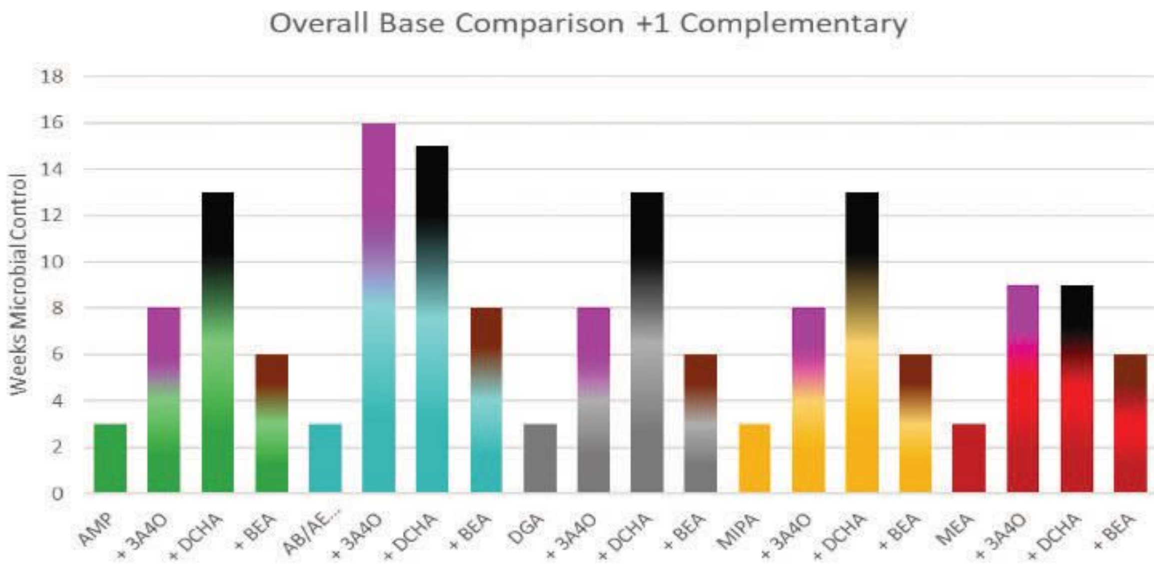

Figure 3. **Introduction of the specialty amines shown to each of or a combination of the amines shown in Figure 2 led to an improvement in the microbial control for specific versions of the semisynthetic fluid. (Key: 3A4O: 3-amino-4-octanol, DCHA: dicyclohexylamine and BEA: butylethanolamine).** *(Figure courtesy of ANGUS Chemical Co.)*

been prepared through the reaction of natural phenolics such as thymol and fatty acids.[9] We believe that the combination of a phenolic structure that shows biocidal properties and the branched nature of the fatty acids that improves the bioresistant characteristic of an additive leads to a promising biocide. One benefit of these compounds is that they are odorless in contrast to currently used phenolic derivatives."

Wagner continues, "Initial testing has shown that poly-phenolic branched-chain fatty acids exhibit antimicrobial properties in testing against the Gram-positive bacterium *Listeria innocua*. Further testing needs to be done with microbes present in MWFs."

Falk says, "Biocide options for MWFs are well understood in today's market. That being said, registration of new biocides specifically for the MWF industry is very unlikely. There is an extremely high cost barrier with biocide-related registrations, and it is unlikely that the MWF market will bear higher pricing for such materials."

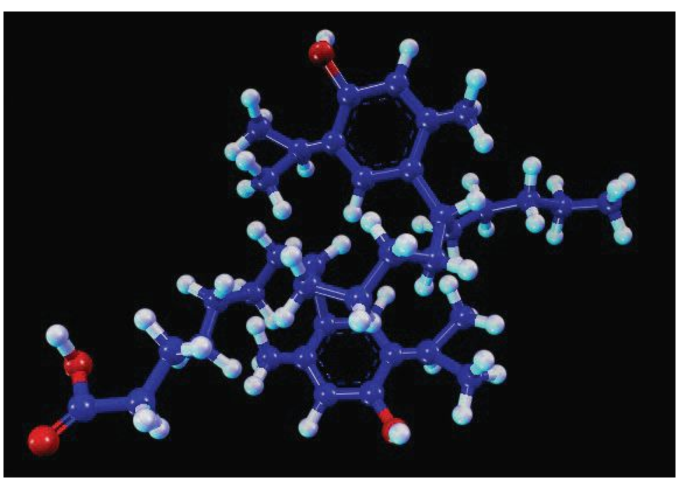

Figure 4. **The proposed structure for a poly-phenolic branched-chain fatty acid is shown.** *(Figure courtesy of the USDA.)*

Passman says, "ASTM E2169 (Tables 1 and 2) lists the currently approved biocides in the U.S. and in the EU. Some of the newer isothiazolinone chemistries (such as BBIT) show promise. Two formaldehyde condensates, MBM and methylene bis oxazolidine (MBO), have the potential of becoming workhorse products if regulators figure out how to distinguish between chemistry and toxicology on one hand and hysteria-driven decision making on the other. Historically, hysteria has trumped science."

Eachus believes that less well-known biocide options may include candidates from cosmetic preservation such as phenoxyethanol and the range of para-hydroxybenzoic acid esters (parabens), as well as benzoates, sorbates and propionates. These materials would show more utility as tankside additives rather than being incorporated into concentrates, and none of them are as robust as the currently used spectrum of MWF preservatives. For this reason, this may entail the need for using higher levels of these other biocide options."

Non-biocide, non-amine additives

With relying solely on biocides to contribute bioresistance to MWFs becoming more challenging, consideration should be given to developing formulations with additives that are harder to degraded by microbes. Most additives used to provide such functions as corrosion inhibition, emulsification and lubricity are derived from linear chain organic derivatives. They are easily consumed by microbes.

Branched alternatives such as isostearic acid can be considered because they are more resistant to microbial attack. STLE-member Dr. Helen Ngo, research chemist with USDA in Wyndmoor, Pa., reported in a past study[10] that isostearic acid with the branched methyl group present at various locations along the alkyl chain will not degrade as readily as the linear stearic acid when exposed to three strains of the bacteria *Pseudomonas*. She says, “While degradation was slowed down, we found that 50% of the isostearic acid with the branched methyl group still degraded in the presence of the bacteria after a 48-hour exposure at 30 C.”

Eachus says, “It is known that linear carbon chains are more readily biodegraded than branched chains such as isoalkanes, and that longer chains are less-readily biodegraded. This has led to the concept of using branched-chain fatty acids to prepare soaps and esters useful as bioresistant surfactants in MWFs.[11,12] The concept of branched-chain versus straight chain hydrocarbons can probably be extended to their use in fatty amines, petroleum sulfonates and other scenarios.”

Byers says, “Formulators should try to select raw materials that are resistant to microbial attack such as branched chain or cyclic molecules, as well as evaluating the use of undecylenic acid and undecanedioic acid.”

According to Clarkson, certain additive chemistries are less accessible food sources for microbes. However, the size and structure of these additives are rather large and cumbersome for microbes to digest, which also makes them more difficult to incorporate into formulations. Clarkson explains, “Other options for helping control microbial growth include large changes in salinity or filtration, but these bring their own challenges related to overall fluid performance and ease of application in a MWF system. A more simplistic option that would preserve performance and not affect filter placement could potentially be the use of temperature.”

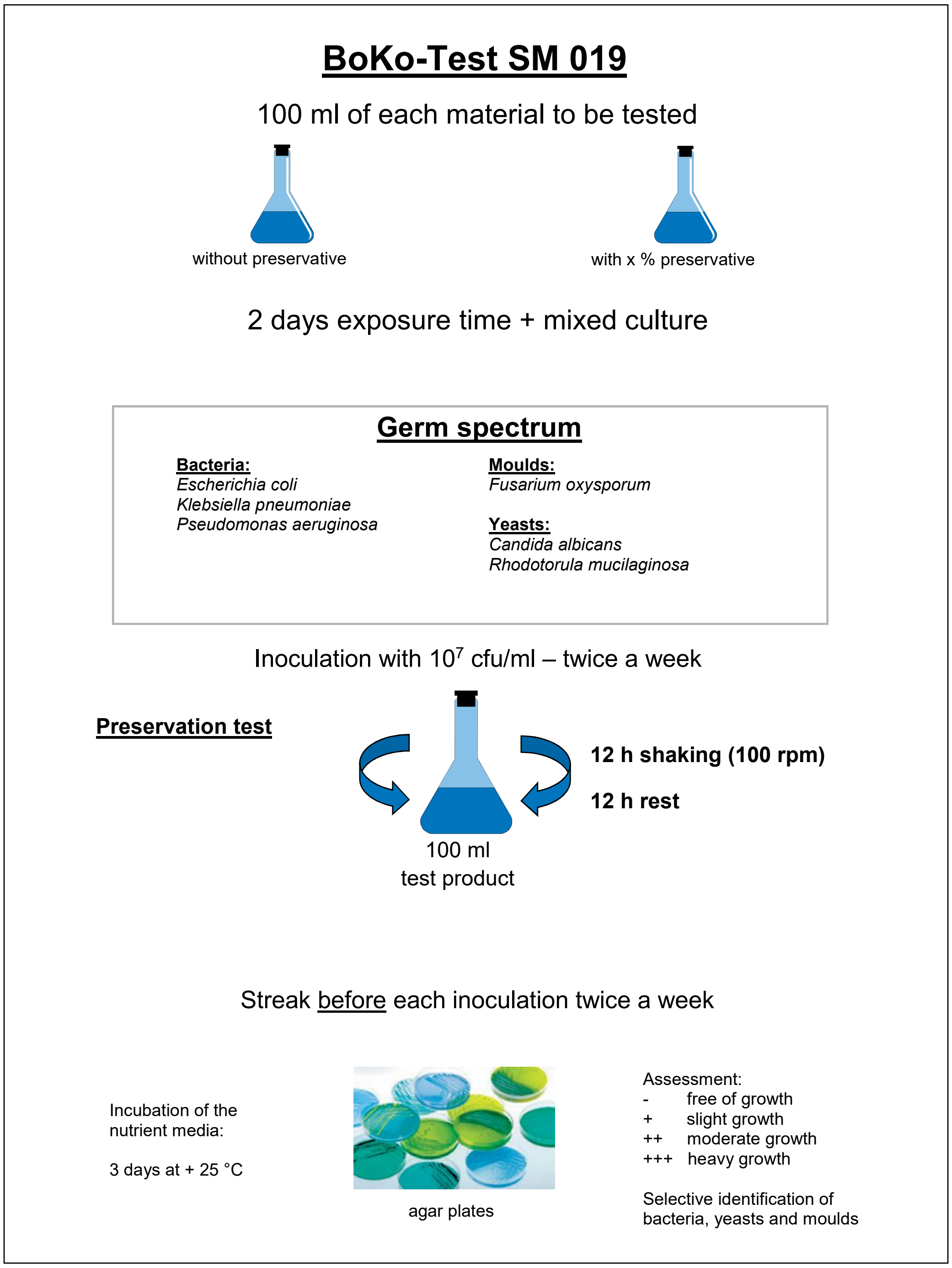

Figure 5. **A procedure known as the BoKo-test is used to determine the bioresistance of a MWF.** *(Figure courtesy of Schülke & Mayr GmbH.)*

Testing

All of the respondents recommended that ASTM E2275 be used to evaluate resistance to microbial growth. Passman says, “Formerly a standard test method, ASTM E2275 is now a Standard Practice—it allows for some flexibility in test setup: static aerated jars, recirculating

No single MWF formulation approach will guarantee success.

MWF microcosms, etc. Keep in mind that minimizing microbial growth reflects bioresistance, not biostability. ASTM E2275 is flexible enough to be used to test for biostability, but for this testing, the focus should be on rates of key component concentration changes, or pH, or performance property loss (for example corrosion inhibition) instead of bioburden data."

The industry representative says, "The first test should be to confirm contamination of a control fluid without addition of biocide. Assuming that this control MWF can contaminate easily, a regular challenge test should be run. In this case, a weekly inoculum of microorganisms is added to the aliquot of MWF coupled with a weekly enumeration to evaluate the biocide's efficacy in controlling organisms in the field. Other options to contaminate the control sample include diluting further than generally recommended, adding a nutrient source to the fluid or repeated inoculums in the space of a few days to two weeks to see if the control can be contaminated."

Curtis says, "Typically, testing is run in comparison to both negative (unpreserved MWF concentrate) and positive controls. The latter can be the existing product where improved bioresistance is the aim or another product for which field performance is well established."

Byers cautions, "In using microbial challenge testing, organisms isolated from used MWFs should be used rather than obtaining organisms from a culture supply house."

Eachus says, "Standard laboratory test procedures such as ASTM E2275 and ASTM E2694 (Standard Test Method for Measurement of Adenosine Triphosphate in Water-Miscible Metalworking Fluids) using, as much as possible, the microbial species expected to be encountered in real-world use should be employed. However, testing under controlled conditions should be confirmed by actual field testing wherever possible."

Ash says, "Microtiter assays to screen individual compounds versus pure strain microbes should be used. Careful and meticulous recording of the normal observations of fluid performance needs to be done."

Sakulowski says, "The Technical Guidance of the BPR mentions the standard test methods IBRG FFG 16-001.5 and ASTM E2275 for determining microbial efficacy. We also run an in-house test procedure known as BoKo-test *(see Figure 5)*. The first part of the test involves performing a microbe count reduction test with the addition of different biocides. Bioresistance of the MWF is then determined through inoculating samples 12 times with a mixed spectrum of microbes."

Formulator view

Kosalko was asked to comment on the current state of options available for formulating bioresistant MWFs. He says, "The battle with microorganisms is a perpetual dance between effective chemistry and regulations that restrict their usage. What is available in your toolbox varies significantly from region to region with the U.S. having more options than Europe. There are many MWF fluids currently on the market that do a good job controlling biological growth, which would suggest that the current options available to formulators are satisfactory."

Challenge testing is the preferred method for both individuals to evaluate bioresistance. Kosalko says, "The major downside to challenge type tests is the time investment that can range from weeks to months before completion. Assuming the matrix is representative and the test is performed with relevant species, the challenge tests can differentiate product performance."

Kosalko continues, "These tests show good but not great correlation with field results. The reason is that no test can incorporate the many uncontrollable variables a MWF experiences in a typical process. There is no test that can effectively predict the impact of contamination of various soil sources, species variation, poor system control, etc.

Additional steps

All of the contributors recommend that good hygiene, good housekeeping and frequent monitoring of MWF systems are essential to minimize microbial growth. Eachus summarizes, "In addition to choosing suitable biocides and additives as ingredients of their MWF formulations, manufacturers must continue to educate their customers, the end-users, on steps which can be taken in the ship to improve fluid longevity. These would include but are not limited to: the use of quality water, maintaining good housekeeping and plant cleanliness; prompt removal of contaminants from working fluids; cleaning the system when fluid is changed out; and using the correct use-dilution specified by the supplier."

Falk lists three steps that should be taken to minimize microbial growth.

1. Establish good hygiene standards in plants to avoid all types of contamination of in-use fluids.
2. Practice frequent fluid monitoring to gauge levels of bacteria/fungi, tramp oil, pH and concentration.
3. Apply appropriate and prompt responses to monitoring data.

Passman says, "Predictive maintenance is the best approach for minimizing microbial growth through the use of best practice, condition monitoring. Microbial contamination should be monitored using a real-time test such as ASTM E2694 because bioburdens in MWFs begin to change shortly after samples are collected. Consequently, the sooner a sample is evaluated after collection, the more accurate the test results. Culture test paddles also can be used but will only support the growth of a fraction of the different types of microbes in a MWF sample. Recent studies using genetic methods have shown that culture tests detect <0.1% of the population."

Passman continues, "Early corrective maintenance, i.e., predictive maintenance, actions are more cost effective because microbes tend to thrive in heavily contaminated MWFs. Ensuring that MWF and MWF systems remain clean pay the greatest dividends. Keeping water hardness to less than 100 ppm calcium carbonate also is an important element in controlling bioburden accumulation."

Byers says, "Besides biocides, MWF formulators should try to identify ingredients that are themselves resistant to microbial attack."

The future

Curtis says, "We do not anticipate significant change in the use of biocides in the short term. A key issue facing all biocide suppliers is the continuing regulatory costs associated with maintaining product registrations. Some product labels now limit the product application to MWFs used in enclosed or semi-enclosed systems. These limitations reduce potential operator exposure and may mitigate some of the high-cost data requirements to support continuing product registrations. Users may see this type of label restriction more frequently in the future."

Falk says, "The use of best maintenance practices and additives with less bioavailability will reduce the need to add biocides. However, biocides will likely still be needed to maintain long fluid life for the foreseeable future."

Sakulowski says, "Even if we see some trends in the direction of 'biocide free,' MWFs will always be in need of biocides because systems provide ideal growing conditions (warmth, nutrients and water) for microorganisms and there will always be contamination."

Ash says, "We predict continued use of biocides and specialty amines with steady growth unless something dramatically better, cheaper and safer is found. Biocides and amines of course may continue to face some regulatory scrutiny."

Clarkson expects that future use of specialty amines will increase as formulators look to maintain fluid performance while available biocide options continue to decrease with the environmental health and safety changes occurring in conjunction with updated Global Harmonized Standard (GHS) labeling/classifications.

Passman warns, "Regulatory pressure will drive down biocide usage until the incidence of respiratory disease increases to a breaking point, after which biocide use will increase. Fortunately, two potentially mitigating factors (increased use of bioresistant MWF additives reducing the need for biocides and better ventilation and mist collection at metalworking facilities) may be sufficient to prevent a recurrence of large clusters of workers suffering from respiratory disease."

Byers says, "As the EPA continues to reduce the number of registered biocides available and reduces their allowed usage levels, formulators will be researching chemistries that kill microbes without actually being EPA registered for that purpose."

Eachus says, "Formulators will rely more heavily on non-biocidal additives, as regulatory pressures continue to deplete the ranks of permissible active antimicrobials. The possibility exists that some suppliers may be able to offer fluids formulated with regionally acceptable components until biocide restrictions become universally adopted. Alternative methods such as dry machining and once-through fluids may become more attractive as prices escalate for fluids made from permitted components."

The quest for bioresistance will continue in earnest. MWF formulators faced with using fewer biocides at lower treat rates will rely on combinations of the available biocides to provide the maximum benefit. Specialty amine use will continue to extend the operating value of biocides. But MWF formulators also will increasingly need to use components that resist microbial attack as a means to extend fluid life. No single MWF formulation approach will guarantee success because applications and end-use operating conditions are too diverse. To ensure that MWF formulators will perform up to producer expectations, end-users must conduct proper maintenance that includes condition monitoring as their best strategy to minimize microbial contamination.

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