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TLT

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SPECIAL ISSUE

Metalworking Fluids

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You've come to the right place for MWF resources

STLE offers a plethora of industry education and training to expand your technical knowledge.

WELCOME TO THIS SPECIAL ISSUE OF TLT devoted to those who manufacture, sell or advise customers on the safe and effective use of metalworking fluids (MWFs) in industrial applications.

Today's MWFs are, in fact, sophisticated materials. All they have to do is provide lubrication, cooling and corrosion control to help machine or form parts at the highest rate of speed, maximize tool life and minimize downtime with the fewest possible rejected parts, all while maintaining dimensional accuracy and finish requirements.

STLE has always been well-respected in the industry for providing a vast array of resources to members that are involved in this critical market. As such, some of the leading experts in the field serve on several active committees in this area, including STLE's MWF Technical and Certification Committees.

In this issue, we've assembled eight "best of" articles ranging on a variety of topics that are sure to help upgrade your technical knowledge, advance your career and help to better serve your employers and customers. This issue is also available to download for *free* online through the STLE Store at **www.stle.org**, making it easy for you to access it anytime or recommend to friends and colleagues.

But your education doesn't stop here. STLE offers other MWF-related programs and services such as world-class education courses at our annual meeting, as well as a two and a half-day certificate program that provides a comprehensive overview of the latest metalworking fluid management best practices and techniques designed to improve your operations.

Not to mention, there's the best-selling book, *Metalworking Fluids, Second Edition*, edited by renowned industry expert Jerry Byers, a past president of STLE. This well-written book is widely considered the technical bible on MWFs and has been translated into a Chinese edition. It definitely should be on the highly recommended reading list for anyone interested in the metalworking industry.

More important, the best way to verify your expanded technical knowledge and demonstrate your professional dedication to the field is by becoming an STLE Certified Metalworking Fluid Specialist™ (CMFS). This special designation verifies the expertise of those involved with research, evaluation, selection, technical management and handling of MWFs. STLE offers a body of knowledge to help you prepare for this challenging exam.

You can find extensive information on all of these of resources at **www.stle.org**.

STLE hopes you find this special issue to be a valuable reference for establishing best practices in your daily work environment.

Dr. Robert M. Gresham
Director of Professional Development
Society of Tribologists and Lubrication Engineers
Park Ridge, Illinois

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Monitoring metalworking fluids

A host of testing methodologies can extend the life of your fluids—and your customer's machinery.

KEY CONCEPTS

- MWF monitoring is extremely important to optimize performance and extend fluid life.
- The most important test is concentration because fluid systems are not static and individual formulation components deplete at different rates.
- Some tests used to monitor MWFs need to be upgraded to shorten the analysis time and improve accuracy and precision.

METALWORKING FLUIDS (MWFs) CAN BE COMPLEX FORMULATIONS CONTAINING A VARIETY OF ADDITIVE TYPES to ensure optimum performance. Among the functions expected of MWFs are providing lubricity, cooling, corrosion protection, prevention of welding and flushing metal chips.

The types of additives used in a MWF are listed in Table 1. Much is expected of the fluid even before a consideration is made about its operating environment. Contaminants such as microbes and tramp oil easily can enter MWF systems and will accelerate degradation over time.

For this reason, it is important to monitor the condition of a MWF over its operating life to ensure the performance can be maintained at as high a level as possible. An assessment of the test procedures used to evaluate MWFs is provided in this article from the standpoint of the additive supplier, MWF formulator, testing lab and end-user.

With the complexity of MWF systems and problems, a large number of tests covering a wide range of parameters can be run. Some of the key tests are shown in Table 2. This article reviews tests used to monitor MWFs and focuses on the development of several new procedures that can provide more accurate data in a faster time frame.

Among the functions expected of MWFs are providing lubricity, cooling, corrosion protection, prevention of welding and flushing metal chips.

CONCENTRATION

STLE-member Andy Nelson, president of ANR Engineering Ltd. in Perrysburg, Ohio, says, "MWFs in general are a compromise both in their formulation and application. On the most basic level, a water-miscible MWF is a compromise in that it must be a stable concentrate capable of being stored at high temperature in Nevada and on a loading dock in Minnesota in the middle of winter. In spite of these temperature contrasts, MWFs must still exhibit the desired characteristics after further dilution with water."

Nelson then indicates the challenges for a MWF during continued use: "When the fluid is applied (most end-users want only one or at most two fluids for the whole shop), the end-user asks that 3 to 10 percent of the concentrate convert water into this magic fluid that will optimize the performance of heavy-duty broaching, high-velocity turning and Blanchard grinding. To have any hope of success, it is critical that the fluid be maintained at the proper concentration."

It is also critical to understand that these fluids fulfill many different functions, including improving surface integrity and the metal-removal process, moving chips out of the cutting zone and providing in-process corrosion protection. The non-cutting considerations include things such as residue characteristics, length and type of corrosion protection, working odors and mists, biological stability, chemical content and disposability, just to name a few. MWFs seldom accomplish just one function.

To determine the optimum working concentration for a specific fluid and a specific operation, it is necessary to do a series of experiments and/or go by previous experience. Nelson says, "Controlling the concentration is critical, and to control anything you must be able to measure it. The problem with measuring MWF concentration starts once the concentrate is diluted with water prior to use."

Table 1 | **MWFs can be formulated with the wide range of additives shown. Additive selection is based on fluid type and application.** *(Courtesy of Chemical Solutions)*

Main Types of Additives Used in Metalworking Fluids

- **Metalworking fluids require a large number of additive types**
- **Antimicrobial pesticides (biocides)**
- **Antifoams**
- **Boundary lubricity additives**
- **Corrosion inhibitors**
- **Coupling agents**
- **Dyes**
- **Emulsifiers**
- **Extreme pressure additives**
- **Metal deactivators**
- **Reserve alkalinity boosters (amines)**
- **Wetting agents**

Table 2 | **Some of the key tests used to monitor MWFs and the parameters they measure are shown.** *(Courtesy of Chemical Solutions)*

Some of the Tests Used to Monitor Metalworking Fluids

Test:	Parameter Measured:
Refractometer	Concentration
Alkalinity Titration	Reserve Alkalinity
Cationic Titration	Anionic Emulsifers
Acid Split	Oil Content
pH Meter	Fluid pH
Four-Ball Test	Extreme Pressure and Wear Characteristics
Culture Methods	Microbe Population Density

Nelson believes the individual components in the MWF start to deplete at different rates, so exactly what the concentration is becomes a guesstimate. "Additionally, these fluid systems are not static and are in a constant state of change," he says. "It is therefore critical that the concentration of the system be closely controlled, and to do that it must be accurately measured.

There are basically four ways of checking concentration: measuring the refractive index of the mixture; titrating for alkalinity, sulfonate or some other property; acid or salt split; and depletion analysis or the measurement of the individual chemical components in the fluid. They each have advantages and disadvantages.

Nelson says, "Measuring concentration by refractometer is fast, easy and can be conveniently done on the shop floor. The conventional analog refractometer does a pretty good job of estimating concentration and provides additional subjective information about tramp oil and emulsion stability. The newest generation of digital refractometers is both more accurate and much more repeatable than analog refractometers."

In addition, digital refractometers have their own light source and evaporation shield and measure the light as it refracts off of the surface of the fluid. This means that many of the sources of error have been eliminated in these new instruments.

In a given application, the MWF is designed to operate at a specific concentration range recommended by the supplier.

'Controlling the concentration is critical, and to control anything you must be able to measure it.'

Nelson says, "In an average machine shop, an end-user will use a refractometer to check the concentration of MWF systems maybe once a week, which is often not enough!"

A refractometer measures concentration by determining the refractive index of the fluid. The primary type used is an analog unit (*see Figure 1*). Light is exposed to a drop of the MWF placed on one side of a glass prism. The light moves through a prism optical wedge and is then focused by a lens on a number scale read by the user. The reading represents the ratio of the velocity of the light moving through the sample as compared to the light moving through water.

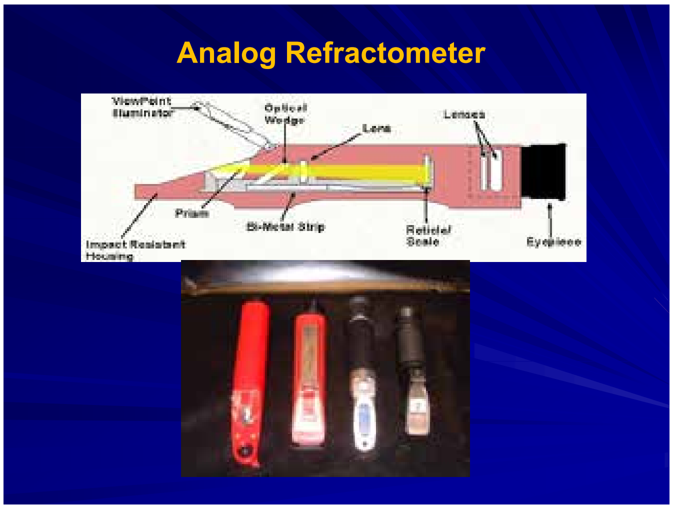

Figure 1 | **Analog refractometers provide an easy and rapid way to measure the concentration of MWFs.** *(Courtesy of STLE)*

Lab bench and hand-held units are both available. Nelson indicates that it is important for the refractometer to have temperature compensation. There is an indirect relationship between the reading and temperature. Nelson says, "Some cheaper, hand-held refractometers may not include temperature compensation."

Calibration of the analog refractometer is also important but is usually done only after the first time the unit is used, Nelson says, while manufacturers recommend calibrating before each use. This can lead to very inaccurate concentration measurements.

An analog refractometer does have some disadvantages. Nelson adds, "Measurement of concentration is less effective when the MWF is contaminated with tramp oil and operates under hard-water conditions. The number scale may also be blurred, making an accurate reading difficult."

Third-generation digital refractometers (from suppliers such as MISCO) have recently become available to the MWF industry over the past few years.[1] Nelson says, "Digital refractometers are better able to handle measurement of MWF concentration under more adverse conditions. A sample is placed in a well and the reading made from below. This method reduces the interference of tramp oil, which floats to the top of the sample."

The digital unit generates a specific value so the user does not have to use an internal scale to determine the concentration. An additional benefit is that the digital unit can be programmed so that the value obtained is the actual concentration of the fluid. In the analog refractometer, the value determined from the internal scale is measured in Brix and must be converted to a concentration figure through a scale, factor or chart provided by the MWF supplier.

The digital unit is equipped with temperature compensation sensors and will not take a reading until the fluid temperature is equal to the temperature of the stainless steel housing that holds the sample. Nelson also indicates that the unit does a better job of minimizing problems with water evaporation than an analog refractometer.

Both lab bench and hand-held digital refractometers are available for use. Figure 2 shows a hand-held unit.

Figure 2 | **Digital refractometers are better able to handle the measurement of MWFs under more adverse conditions. They also provide better accuracy and precision than analog refractometers.** *(Courtesy of MISCO Refractometers)*

The accuracy and precision of a digital refractometer is between +/- 0.1 and 0.2 Brix units. The best analog units have an accuracy and precision of +/- 0.2 Brix units.

Nelson offers a case study that examines the value of using a digital refractometer. The study involves an emulsified oil containing a high level of tramp oil. The virgin fluid is diluted to an initial use concentration of 10%.

Nelson explains, "In this particular case, the amount of tramp oil entering the MWF system increased to the point that it represented 90 percent of the total MWF content. The end-user was confused because he was told his problem was not due to concentration."

He continues, "The analog refractometer could not provide an accurate reading because the internal scale was fuzzy. In contrast, the digital refractometer was much more effective and provided accurate concentration readings up to levels of 50 percent tramp oil."

WET CHEMICAL AND INSTRUMENTAL TESTING

While a refractometer is the most important test to monitor the condition of a MWF, other procedures are used to examine specific fluid components. Tests can be placed into the categories of wet chemical titrations, instrument analysis and performance tests.

The first category covers the evaluation of the acid number and reserve alkalinity of the MWF and the determination of the content of anionic surfactant through an actives titration. A test that also can be placed in the wet chemical category is to determine oil content through treatment of the fluid with mineral acid. This acid split technique provides a quantitative measurement of free and entrained mineral oil.

The reserve alkalinity, anionic surfactant determination and acid split tests provide a measure of the concentration of specific components used in formulating the MWF. They complement the results obtained from the refractometer.

The primary instrument test is a pH meter to determine the pH value of a water-based MWF. Most MWFs are designed to operate at a pH range around 9. Deviations from this value will indicate to the user that the MWF is facing contamination and may be starting to deteriorate.

Instrument analysis determines if a specific component in a MWF has been depleted or if a new component is present that might suggest the fluid is starting to deteriorate. Testing methods include:

- Infrared analysis, which looks for specific functional groups in the components formulated into the MWF.
- X-ray fluorescence, which focuses on detection of specific elements such as sulfur, chlorine and phosphorus.
- Elemental analysis by such techniques as inductively coupled plasma (ICP) that detects a wide range of metals that may be contaminating the MWF.

Performance tests evaluate a specific property of a fluid such as its extreme-pressure characteristics, foam profile and corrosion protection. The first parameter can be measured through the use of a machine such as the Pin and Vee Block or Four-Ball tester. Foam is a critical characteristic, and there are a variety of techniques used to evaluate it, including shake foam, recirculation and wear blender tests. Corrosion protection is evaluated by use of the cast-iron chip test.

Figure 3 | **The Multi Four-Ball Test Machine incorporates both the four-ball EP and wear testers into one computer-operated instrument to measure the extreme-pressure and wear properties of a MWF.** *(Courtesy of Engineered Lubricants Co.)*

Further details on these tests can be found in the book *MWFs: Second Edition*, published in 2006.[2]

With a wide variety of tests and a large number of MWFs used in the marketplace, the question of which tests to use for a specific MWF in a particular application comes to mind. Chris Fink, lab manager for Engineered Lubricants Co. in Maryland Heights, Mo., says, "In evaluating MWFs, it is important to know what fluid type is being examined. We have two basic formats. There is one for oil-based products and one for water -based products."

For oil-based MWFs, Fink indicates that his lab has a basic testing format. "We evaluate oils for viscosity, total acid number, copper strip test, infrared analysis, elemental analysis (by ICP and XRF) and wear analysis using the Multi Four-Ball Tester," he says. An image of the tester is shown in Figure 3.

Performance tests evaluate a specific property of a fluid such as its extreme-pressure characteristics, foam profile and corrosion protection.

Some of the same tests (infrared analysis, four-ball wear testing and elemental analysis) also are useful for water-based fluids. Fink adds, "We find that determination of pH, cast-iron chip testing, foam testing and metal coupon testing also are required."

In assessing the potential performance of a new MWF, Fink indicates several tests are very useful to predict performance. "Elemental analysis, an infrared scan and wear test-

Evaluation of a used MWF is more complex because there could be a number of reasons why the fluid is not performing at an optimum level.

ing are the most valuable tests," he notes. "These analytical tests give a quick basic look at the structure of the product and how it performs in the field."

Evaluation of a used MWF is more complex because there could be a number of reasons why the fluid is not performing at an optimum level. Fink says, "The concentration ratio in water-based fluids and the combination of pH, bacteria and fungal dip slides, ICP and the cast-iron chip test give a good indication of the condition of the used fluid. However, it is best to set the system up on a routine sampling schedule so you can track the life of a MWF. In this way, a customer can maintain the fluid under optimum conditions."

Fink offers an example of how several tests were needed to solve a specific MWF problem. "Recently, we had a customer using an oil-based chlorinated product for stamping and forming cold-rolled steel and aluminum parts," he says. "Their problem was staining and rusting of stacked parts."

The customer perceived that a non-chlorinated product would be needed, so the challenge was developing a product that maintained the extreme-pressure performance of the current product while eliminating the stain and rust problems. Fink indicates that several test procedures need to be run in the development of a new product.

"We needed to try several extreme-pressure additives in combination to achieve this goal while maintaining the same product viscosity," he says. "Numerous tests were run on the Multi Four-Ball tester to find the proper combination and concentration of extreme-pressure additives. In addition, corrosion testing was conducted in the humidity cabinet to ensure that the product did not stain or rust aluminum and steel parts."

MICROBE POPULATION DENSITY

Determining the extend of microbial contamination in MWF systems is a priority because microbes such as bacteria and fungi are known to not only cause MWFs to decompose, leading to premature failure, but also to cause health and safety problems. Many of the problems faced by end-users are discussed in a previous TLT article.[3]

An example of how microbes can cause problems is the image of the formation of a biofilm shown in Figure 4. Biofilms are communities of microbes that become established on MWF system surfaces to utilize the components of the fluid as food.

STLE-fellow Dr. Fred Passman, president of BCA Inc. in Princeton, N.J., says, "This biofilm was found on the wall of a sump just above the MWF surface. In this zone, MWF splashes onto the sump walls, replenishing water and nutrients that enable the microbes to continue growing. The biofilm continues along the tank wall below the MWF surface."

There are a number of test procedures used to measure the population density of microbes. Passman says, "The primary test is to culture the microbes by adding a sample of the fluid to a dip slide and then incubating it. Over time, the microbes present will grow, and the user will then see the extent of fluid contamination."

This test is easy to use and inexpensive to run. Both bacteria and fungus can be detected as the dipslides contain media to grow both microbes. The microbes form colonies that are detected by the user. Results are reported in colony-forming units per milliliter. Passman says, "One of the biggest problems with the test is that it can take at least 24 hours and sometimes a week or longer to detect colonies. Each colony represents a billion cells or 30 generations of microbes."

In many cases, MWF end-users need results much more quickly. Three other tests provide faster feedback. The catalase test introduced in 1981 measures the amount of oxygen gas generated when a MWF sample is treated with hydrogen peroxide. Catalase is an enzyme known to be present in aerobic bacteria and all species of fungi.

Passman says, "The amount of oxygen generated is roughly proportional to the biomass in the sample. This test can be conducted in 15 minutes, either in a lab or at the location of a MWF system but does not distinguish between bacteria and fungi."

Figure 4 | **Microbes can cause problems in MWFs systems by forming biofilms such as the one found here on the wall of a sump just above the MWF surface.** *(Courtesy of BCA Inc.)*

A second technique involves measuring the change in the amount of dissolved oxygen in a MWF sample after shaking it. Passman says, "I prefer to let the sample sit for two hours and then measure the change in the dissolved oxygen concentration. This test can be performed in the field, but it also only detects aerobic microbes and does not differentiate between bacteria and fungi."

A third test measures the concentration of adenosine triphosphate (ATP), the main energy carrier present in all living things. In a manner of only a few minutes, a new procedure has recently been developed to measure the concentration of ATP in a MWF sample.[4] This technique was developed by the Canadian company LuminUltra™ Technologies Ltd. in Fredericton, New Brunswick.

Figure 5 | **A new ATP test has just been approved by ASTM to measure the microbe population density in a MWF system.** *(Courtesy of LuminUltra™ Technologies Ltd.)*

The procedure takes advantage of the reaction of ATP with the enzyme substrate complex Luciferin-Luciferase. Passman comments on the procedure, "The ATP test provides data as quickly as many of the tests that have been used historically to do MWF condition monitoring. This translates into an opportunity for real-time control and substantially more cost-effective fluid management. Because it detects all metabolically active microbes in the sample, it provides an accurate measure of both total biomass and the biomasses biodeteriogenic (damage-causing) potential."

The ATP test has been approved by ASTM and is designated as E2694. This method can be run both in the lab (*see Figure 5*) and in the field. A full interlaboratory study during which 10 participating companies tested 22 emulsifiable oils, semisynthetic and synthetic MWF samples was recently completed. The results, which show excellent repeatability and reproducibility, will be reported in a manuscript being prepared for publication in STLE's peer-reviewed journal, *Tribology Transactions*.

Passman anticipates that a polymerase chain reaction (PCR) field method may become available sometime within the next decade. PCR creates many copies of specific DNA fragments. This technique can be used to prepare and analyze genetic material from the various microbes present in a sample. Once identified, the user will then know which microbes are present.

Passman says, "PCR methods are continuing to evolve at a good pace. A reliable field method may be available for use in the future. For now, PCR requires expensive instrumentation and skilled technicians to perform. Keep in mind that it took nearly 60 years to get the ATP test from its original form to one usable for MWF analysis."

ANALYSIS OF SURFACTANTS

For most water-dilatable MWFs, particularly those that form emulsions, surfactants are key components needed to stabilize the formulation. With the many different types of surfactants available, it can be difficult for a MWF formulator to determine how to evaluate them if they run into formulation or performance problems.

STLE-member James Stephens, business manager for Clariant Corp. in Mt. Holly, N.C., says, "Surfactants are diverse, which makes it very difficult to evaluate them. We evaluate their properties from both an instrumental and a wet chemical standpoint."

Instrument testing includes multinuclear NMR (nuclear magnetic resonance) analysis, infrared analysis, HPLC (high pressure liquid chromatography) and GC/MS (gas chromatography/mass spectroscopy). Stephens adds, "We utilize proton, carbon-13 and phosphorus-31 NMR because these techniques help to determine the structure of the surfactants."

HPLC and GC/MS are both separation techniques, especially useful at detecting contaminants in surfactants and, as a consequence, assessing their purity. Both methods involve mixtures in a mobile phase passing through a stationary phase. Components in the mixture travel through the stationary phase at different rates, thereby becoming separated. In HPLC the mobile phase is a solvent or solvent mixture, while for GC/MS the mobile phase is a gas such as nitrogen. An added value of the latter technique is that the isolated components can be analyzed by mass spectroscopy to expedite their identification.

Besides acid number, wet chemical procedures used to examine surfactants include cloud point, hydroxyl value and saponification number. Cloud point is a particularly useful method that evaluates the solubility of a surfactant in water, salt solutions and various solvents. This parameter is defined as the temperature at which the surfactant becomes insoluble in a specific solvent.

Hydroxyl number and saponification value are both used to determine the extent of the reactions of specific esters, a major class of nonionic surfactants. The former is also used to assess the composition of other nonionic surfactant types.

The time-consuming and variable nature of several of these techniques has led to upgrades that improve accura-

Other variables that need to be checked in high-speed machining include the tool holders, tool materials and MWF.

cy. Stephens says, "Determination of hydroxyl numbers is a time-consuming process that can be replaced with in-process near infrared analysis. Cloud point testing also can be very subjective depending upon the operator. We have found that instrument analysis using light transmittance has minimized variability."

For field problems with surfactants, Stephens looks to work with a number of techniques to check composition and for contaminants. He says, "We first start with a basic infrared analysis. Additional testing by GC/MS easily can detect any impurities or contaminants. We also look at various NMR techniques to check for structural irregularities."

MACHINING TESTS

The prior test methods discussed are used to evaluate the MWF or components incorporated into the MWF. There are also test procedures used to monitor the effectiveness of the machining operation.

STLE-member Gary Rodak of Machining Efficiencies, Inc. in Gregory, Mich., says, "Tool wear and surface finish evaluations typically describe the quality of the parts produced. Tool wear patterns identify the overall performance of the machining process. Monitoring tool wear patterns enable the machinist to recognize machine vibrations due to incorrect setup conditions, high heat due to improper aim of nozzles or excessive tramp oils, sediment issues and other suboptimized conditions."

The movement of the MWF industry to high-speed machining was discussed in a past TLT article[5] and presents another set of challenges in detecting machining problems (*see Figure 6*). Rodak says, "In high-speed machining situations, tool chatter is very destructive. The tool wear pattern that indicates chatter is very obvious on the tool edge and in the remaining part micro-finish. A modal analysis test of the rigidity of the machining setup, part and fixture will identify the optimum combination of depth of cut and revolutions per minute that would be suitable for stable machining. An acoustical analysis may indicate when the machine setup is chattering."

Other variables that need to be checked in high-speed machining include the tool holders, tool materials and MWF. Rodak explains, "There is more to high-speed machining than surface speed. The tool holders must be HSK style E or F to eliminate vibrations and tool holders should be shrink-fit style."

He continues, "Tool material and coatings limit the upper temperatures that the cutting tool can tolerate. High-pressure MWF coolant delivered through the tool to the cutting zone keeps the tool edge temperatures in an operable range.

Figure 6 | **High-speed machining is monitored through evaluation of a tool wear pattern, acoustical analysis and a modal analysis test.** *(Courtesy of Machining Efficiencies, Inc.)*

Cryogenic lubricants such as carbon dioxide are being developed to reduce cutting zone temperatures."

END-USER PERSPECTIVE

STLE-member Lloyd Lazarus, staff engineer for Honeywell Federal Manufacturing & Technologies LLC in Kansas City, Mo., is responsible for maintaining MWF in one 7,000-gallon central system and 100-150 machine sumps ranging in volume from one gallon up to 100 gallons. He says, "We need to take care of a large number of MWF systems that contain several different MWF types that are oil- and water-based."

The plant is run on a two-shift, five-day schedule. During off-shifts and weekends, the central system is run for 10 minutes every two hours to minimize the potential for growth of anaerobic microbes.

Many of the operations are done in machine centers that conduct profile and plunge milling, boring, drilling, gun drilling and reaming operations. Lazarus notes that many of the production runs involve small quantities of parts.

In monitoring MWFs, much of Lazarus' attention is spent on the central system. He says, "The refractometer is our primary method for measuring the concentration of the MWF. We check pH when checking concentration. We run an alkalinity titration, do an acid split, determine dissolved oxygen and conduct water-hardness tests using dipsticks on a weekly basis."

With the municipal water having hardness between 80 ppm and 120 ppm and his use of make-up water treated by reverse osmosis, Lazarus does not bother with measuring conductivity. Refractometer, pH and water-hardness dipstick testing is done 2-3 times per week on the central system. The acid split procedure is usually run once a week.

A proprietary biocide test is conducted on the central system to determine the concentration of biocides, bacteria and fungus. This colorimetric procedure is used twice a week. Dip sticks are incubated every two weeks to determine bacteria and mold counts.

For many of the higher capacity, stand-alone machine sumps, concentration is measured by refractometer about once a week. Lazarus indicates that 60 percent of these sumps hold fewer than 50 gallons, so it is not time effective to do additional testing.

One of the most useful tests run by Lazarus is the acid split procedure. He says, "Our central system runs at a high velocity and mechanically retains a lot of oil. We need the data from the acid split procedure to indicate whether excessive oil may have entered the system from a hydraulic fluid leak."

Above all Lazarus stresses the need to keep records on MWFs systems that include all of the data obtained on a daily basis plus any pertinent observations. "The objective is to use this data to pick up trends about the condition of the fluid in order to take action before major problems occur," he says. "In addition, we use this data to make sure we do not repeat mistakes made in the past."

Lazarus maintains that such an approach is really only worthwhile for a large central system. With smaller machine sumps, it is simply not worth it.

In the case of a machinist turning on a small system and detecting an odor problem that may suggest the MWF is spoiled, Lazarus suggests that the sump be run for a little bit. If the odor persists, the system is dumped, flushed and refilled.

UPGRADING TESTS

Some of the current test methodology needs to be upgraded, either because the current procedures are too time-consuming or there are problems with accuracy and precision. In the case of lengthy testing, results are needed very quickly so that the appropriate measures can be taken to address a specific MWF system problem. Any lengthy delay may serve to only make the problem worse.

Nelson raises concerns about the need for new test methods to evaluate several important parameters used to evaluate the MWF condition. He says, "One of the big issues is finding a way to speed up the procedure run to determine the population density of fungus in a sample." The standard dip slide procedure can take three days to determine if fungus is present and provide a measure of this microbe's population density.

Conductivity is a general measure of the concentration of inorganic cations and anions. Nelson would like a test that provides information about the concentration of more specific cations and anions besides those available to evaluate for hard water (calcium and magnesium ion concentration).

Nonferrous staining is another parameter that cannot be readily predicted. Nelson says, "In machining an aluminum alloy, one problem that can occur is white rust. This problem could occur because of galvanic corrosion between copper and aluminum if both are present in the machined part. The minute copper ions are present in the MWF, the metal deactivator starts to be used until it is exhausted, which triggers the problem. It is not practical to run ICP to determine if copper is present. An alternative test method that can be run at a MWF system is needed."

Fink indicates that too many factors are in play in trying to accurately determine the concentration of a MWF system. He says, "When customers read their refractometer or try a titration at a plant, they find it difficult to compare their answers to our reports from the lab. The customer questions why the ratio is not always the same."

For Lazarus, the acid split is a very important test but just takes too long to run. He says, "The acid split procedure takes three to four hours to complete, which is way too long. Results need to be available more quickly in order to determine if a centrifuge needs to be turned on to deal with excessively high levels of oil. In contrast, measurement of concentration with the refractometer and pH analysis takes only a few minutes."

As the demands to run MWF systems for longer time frames continue, monitoring the condition of the fluid is becoming increasingly important. Newer techniques have been developed that enable more accurate data to be obtained in a shorter time frame. With the complexity of MWF systems, there continues to be the need for developing additional test procedures that can provide data in a faster and more accurate fashion. TLT

REFERENCES

1. Canter, N. (2009), "Greater Accuracy through Digital Refractometers," TLT, **65** (3), pp. 16–17.

2. Byers, J. (2006), "Laboratory Evaluation of MWFs," *Metalworking Fluids, Second Edition*, edited by Jerry Byers, CRC Press, Boca Raton, Fla., pp. 148–173.

3. Passman, J. (2009), "Microbial Problems in MWFs," TLT, **65** (8), pp. 26–34.

4. Canter, N. (2009), "New Test Method for Detecting Microbes in MWFs," TLT, **65** (8), pp. 8–9.

5. Canter, N. (2007), "The Tribological Challenges of High-Speed Machining," TLT, **63** (3), pp. 28–36.

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Jeanna Van Rensselar / Contributing Editor

KEY CONCEPTS

- Biobased MWFs, in some cases, offer superior performance compared to their conventional counterparts.
- Biobased MWFs have a significantly higher flashpoint than conventional MWFs, making them a safer choice for work areas at high risk for fire.
- The proper additive package can increase the performance and extend the useful life of a MWF.

They're playing an expanded role in protecting the environment and offer superior performance in some applications.

The growth of biobased metalworking fluids

To keep up with the growing demand for metalworking fluids that are made from renewable resources, formulators are developing biobased products that, in many cases, perform as well or better than conventional MWFs at a comparable price.

As straight oils, research shows that biobased MWFs can perform significantly better than mineral oils. This is also true to some degree for vegetable stocks emulsified into soluble oil and semisynthetics.

The U.S. Department of Agriculture defines biobased this way: "A product determined by the Secretary (of Agriculture) to be a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal and marine materials) or forestry materials.[1]"

In the case of biobased MWFs, the basestock is most likely soybeans, rapeseeds (canola), sunflowers or corn. STLE-member John Hogan, technical service manager for metalworking additives for The Lubrizol Corp. in Wickliffe Ohio, explains, "When selecting the best vegetable basestock, there are several factors that need to be considered: end-use application of the product, oxidative stability, saturation level and additive selection. Availability of basestocks in different countries, in different seasons and over the long term is important to consider in the initial selection of the basestock."

As with most biobased products, in order for MWFs to perform as well as their non-biobased counterparts, chemicals need to be added that compromise the biobased nature of the fluid to differing degrees.

Hogan says, "The use of renewable resources may be desirable, but that does not necessarily make a product green or sustainable. When evaluating the use of renewable materials relative to petroleum products, lifecycle analysis and total environmental impact must be considered. This means the energy consumed and the waste emissions along the entire spectrum of the product must be considered: gathering raw materials, manufacturing the product, distributing the product, product use and disposal/recycling of a MWF must all be considered in evaluating its environmental impact."

Although biobased MWFs were once a poor substitute for conventional MWFs (offering little advantage other than safety and significant performance disadvantages) new formulations, genetically modified crops and additives are leading to performance that is at least comparable and, in some cases, superior to conventional MWFs. This means that facilities can

[1] [FSRIA, section 9001]

finally use biobased MWFs to protect their workers and improve performance without incurring significant additional cost.

STLE-member Craig Mott, executive vice president of Colonial Specialty Chemical in Tabernacle, N.J., explains, "Market drivers include OEM requirements, Federal government mandates and the green movement. Also, additive/surfactant technology is helping the performance of green fluids; this means there are more vegetable oil options, such as improved oxidation, available for the formulator."

Formulators, distributors and users are confident that biobased MWFs, even with a slew of additives in them, are safer and perform as well or better than conventional MWFs with little price disparity.

In addition to reduced environmental impact, there are genuine performance advantages to using biobased MWFs. But there are still a few issues to be worked out before they become generally accepted (and preferred) alternatives to conventional MWFs.

ADVANTAGES

In addition to helping to protect worker health and the environment, biobased MWFs have a number of performance advantages. Viscosity, lubricity and flashpoint are three areas where biobased MWFs really shine. This is especially true for straight biobased oils and less so for solubles and synthetics.

Greater viscosity stability. Vegetable oil has a high natural viscosity. As the machining temperature increases and as ambient temperatures fall, biobased MWFs tend to hold their viscosity levels better than conventional MWFs.

Better lubricity. Unlike conventional MWFs, biobased oils have a slight polar charge. This charge naturally attracts the oil to metallic surfaces and is resistant to being wiped off. This polarity also leads to better corrosion protection.

Higher flash, fire and smoke points. Biobased MWFs have a significantly higher flashpoint than conventional MWFs—around 200 degrees higher. This makes them a safer choice for all workspaces, especially those that are tightly enclosed and/or near open flames.

Workers at the U.S. Naval Air Depot at Cherry Point, N.C., are seeing the benefits of biobased MWFs every day. There are about 160 machines at the facility using MWFs. After giving a prototype biobased MWF a fair trial, users came to the following conclusions:

- The flashpoints of straight oils used in the past were 350 F to 400 F. The prototype has a flashpoint of 640 F. Because of its high flashpoint, the biobased prototype provides better heat dissipation and produces less smoke when machining.
- The graphite-like material from the molybdenum disulfide source in the prototype allows metals to be processed with less friction and less torque compared to the MWF they were previously using.
- The prototype provides better tool life compared to the MWF previously use.
- Biobased MWFs lead to a safer and healthier environment.[2]

MWF Quick Primer

MWFs have many applications, but all have the basic purpose of lubricating and cooling the work piece-tool interface, flushing scrap and residue from the work area and improving the surface finish on end-products.

MWFs are categorized into the following four classes:

- **Straight/neat/cutting oil.** Ultra-refined oils that are not diluted with water but may contain additives.
- **Soluble oil.** Composed of anywhere from 30 to 85 percent severely refined basestock, water and emulsifiers.
- **Semisynthetic fluids.** Containing 5 to 30 percent severely refined oils, 30 to 50 percent water and several additives.
- **Synthetic fluids.** Composed of compounds that do not contain any petroleum oil.

Each of the four classes also may contain additives such as biocides, corrosion inhibitors, extreme pressure chemicals, defoamers, emulsifiers, stabilizers, dispersants and dyes.

CHALLENGES

Poor oxidative stability, poor hydrolytic stability, microbial growth promotion, warranty issues and higher cost are the five main drawbacks to using biobased MWFs. However, with the right formulation expertise, these challenges are easily overcome.

Poor oxidative stability. This is a significant concern because, among other undesirable effects, it causes expensive tools to wear more quickly. STLE-member Lou Honary, professor and director of the National Ag-Based Lubricants Center, University of Northern Iowa (UNI-NABL Center) in Waterloo, Iowa, explains, "While oxidation stability remains a big concern in most applications where vegetable oils are used, the oils is carried

[2] Naval Air Depot Cherry Point Prototypes Alternative Metal Working Fluid, 2006, summary available at: **http://www.denix.osd.mil/sustainability/upload/DoN_Leadership-in-Biobased-Products-Usage.pdf.**

out with the chips or as a film on the machined part, thus the residency of the oil is shorter in the machine than applications like gear oil or hydraulic oils. Nevertheless, oxidation stability is important because most other attributes like solubility and compatibility with additives are easier to address."

Poor hydrolytic stability. Conventional MWFs are resistant to hydrolytic reactions because they do not contain ester linkages and thus don't hydrolyze (break down). This is not the case with biobased MWFs. The good news is that a genetically modified basestock that is naturally more hydrolytically stable is currently being developed. Other ways to overcome the poor hydrolytic stability are through additives and/or chemical modification.

Microbial growth. Unlike conventional MWFs, biobased MWFs tend to promote microbial growth—the oil biodegrades in the machinery. This compromises performance and creates a noxious odor. The addition of an approved antimicrobial can minimize these problems.

Prohibitive manufacturer warranties. In some cases, using biobased MWFs could void the manufacturer's warranty. The U.S. Department of Agriculture, in an effort to promote responsible use of biobased products, is working with OEMs on the issue of maintenance warranties. Specifically, the USDA has been contacting manufacturers, industry associations and service professionals to request information about and ultimately resolve warranty issues. As additional information becomes available on the project, the USDA will post it on the BioPreferred Website: **http://www.biopreferred.gov**.[3]

Cost. The level of cost disadvantage depends on the basestock. In addition, additives required for equalizing oxidative/hydrolytic stability and microbial growth issues add to the cost. But as petroleum prices continue to escalate and some countries offer tax incentives for using biobased products, the cost differential is becoming less pronounced.

The basestock for biobased MWFs most likely is soybeans, rapeseeds (canola), sunflowers or corn.

Mott says, "As far as the cost of biobased MWFs, when compared to conventional MWFs, there is still a premium, but this gap is narrowing considerably with petroleum trading at $120 a barrel. Vegetable oils have also moved up in price but not as much as petroleum."

FORMULATION

The development of biobased MWFs has been a research focus for scientists at the UNI-ABIL Research Program since 2002. The center has been formulating alternative, biobased MWFs using renewable crop basestock to minimize environmental, health and safety concerns without compromising performance.

Honary says they've discovered that while certain additives like sulfur used for wear protection are effective regardless of the base oil, it may be necessary to use different antioxidants for vegetable oils than those used for mineral oils. The same logic applies to emulsifiers, antibacterials and pH improvers.

He adds that vegetable oils have two main areas that need consideration during formulation and use: oxidative stability and cold-temperature performance. "Since most metalworking applications are indoors, the cold temperature issue becomes relatively irrelevant." Honary explains: "This makes it easier to focus on improving the oxidative stability while formulating MWFs."

Mott says that for water-based systems, emulsion stability is the most common customer concern they hear about. "The end-user cannot tolerate their MWFs splitting out in use," he says. "This is where newer surfactant technology has really helped the formulator. These new surfactants are doing a very good job in keeping the emulsions very stable in both small and large central systems."

Formulation is a complex science. Hogan explains, "Vegetable basestocks normally require somewhat higher emulsifier content with a different hydrophilic-lipophilic balance for water-extendable products. Selection of emulsifiers and sources of alkalinity are important to consider in order to prevent interactions with the basestock over time that can degrade emulsion stability."

"Higher quality, high oleic content basestocks are generally easier to emulsify and yield more stable products," Hogan says. "Longer fatty chains and increased unsaturation generally require higher emulsifier treat rates. Inclusion of antioxidants is essential to limit oxidation and maintain emulsion stability. Selection of the right antioxidant is critical not only for limiting oxidation but also because it can impact aesthetics of the fluid."

He also points out that while there is a great deal of emphasis on the use

[3] 7CFR Part 2902: Designation of Biobased Items for Federal Procurement; Final Rule, 5/14/08, **http://www.epa.gov/epp/pubs/guidance/fr73no94.pdf.**

USDA's BioPreferred Program

The purpose of the U.S. Department of Agriculture's BioPreferred® program is to promote the increased purchase and use of biobased products with the effect of reducing petroleum consumption, increasing the use of renewable resources and better managing the carbon cycle, which may contribute to reducing adverse environmental and health impacts. The USDA BioPreferred program has two major initiatives:

- **Product Labeling.** The USDA certifies and awards labels to qualifying products to increase consumer recognition of biobased products.
- **Federal Procurement Preference.** USDA designates categories of biobased products that are given preference by Federal agencies when making purchasing decisions.

Official audits of biobased products designated as BioPreferred began in March 2012. The purpose of the audits is to ensure the integrity of the voluntary biobased product certification and labeling initiative and the preferred federal procurement initiative. The audits provide oversight and monitoring of the products affiliated with the program to ensure that the products' biobased content information is accurate and meets the requirements of both initiatives.

For more information, visit: **http://www.biopreferred.gov/?SMSESSION=NO.**

For more in-depth information on this topic, check out the STLE Webinar: "USDA BioPreferred Program," presented by Rudy Pruszko (Industrial Specialist at CIRAS, Iowa State University). Archived recording available for purchase at **www.stle.org**. Cost: $39 (STLE members), $59 (non-members).

of vegetable basestocks to formulate green MWFs, there also are additive technologies based on renewable materials. The new additive technologies are designed to provide the lubrication properties of vegetable oils and are easier to utilize in some water-extendable fluids.

Gene Tripp, sales manager for Performance Biolubes in Cedar Falls, Iowa, says, "Finding the right additives and getting them to remain in the formulation are the real challenges. When it comes to additives, the fewer you use the better. The more ingredients you use and the higher quantity only adds to the cost."

Fuchs is a formulator and proponent of synthetic esters. The company's product manager for Cutting & Grinding Fluids, Jonathan Chow, explains: "Variability of supply, hydrolytic stability and oxidation stability have led us to prefer synthetic esters derived from natural vegetable oils. These give much better robustness and consistency. The higher price can be justified by superior performance."

RECYCLING, WASTE TREATMENT AND DISPOSAL

While the term recycling generally refers to collecting and repurposing, when applied to MWFs the term refers to the common practice of continuously treating and reusing MWFs in the machinery. Once the MWF has reached the end of its useful life, it is almost always treated and disposed of—not recycled in the traditional sense. This is due to the fact that, in most cases, it's already been recycled as much as possible in the machinery.

RECYCLING

The goal of any MWF recycling program is to maintain a stable fluid at optimal performance as long as possible. No matter whether it involves conventional or biobased MWFs, the goal is inherently green since it significantly reduces the amount of waste product in the environment. The same benefits of recycling conventional MWFs apply to biobased MWFs as well (reduced use, little or no equipment downtime, etc.). But in the case of biobased MWFs, aggressive recycling also reduces the strain on natural resources such as crop production.

"If the oil is stable, the recycling of vegetable oil can be done the same as that of the mineral oil-based MWFs," Honary says. "That is, using centrifuge or other means of recovering the base oil for reuse." He adds that this is assuming that the vegetable oil doesn't oxidize during use, which could change it to polymer and render it unrecyclable.

MWFs can only be recycled a limited number of times before they reach the point of disposal. The factors limiting coolant recycling are biological hardness, selective depletion and tolerance to water hardness minerals.

TREATMENT

Waste treatment and disposal of spent MWFs involves first removing the water and then isolating the hazardous components. The remaining product is then hauled away for incineration or recycling. Costs of fluid handling can account for more than 15 percent of total machining costs.[4]

When treating biobased MWFs, the following three waste treatment processes used for conventional MWFs apply.

Physical treatment. Various physical treatment methods are used effectively to treat MWFs for disposal. Evaporation is a common treatment for small amounts of oily wastewater—fewer than 3,000 gallons a day. The process uses heat to remove water from the used fluid, which has the effect of concentrating the fluid. While this avoids the necessity for sewer discharge, it may require an air discharge permit. Another common physical treatment method that is best for moderate waste fluid volumes is membrane separation via ultra-filtration or reverse osmosis.

Chemical treatment. Chemical treatment uses inorganic or organic chemicals to destabilize or separate emulsions of MWF waste. From a cost perspective, chemical treatment makes more sense for large volumes of MWF waste. Chemical treatment produces a byproduct that, with further treatment, will recover some fluid. Unlike physical treatment, it will treat and remove metals.

Biological treatment. The high organic content of biobased MWFs makes them excellent candidates for treatment via bacterial degradation. But as with all other MWFs, the high oil content of these fluids means that other methods also must be used. Biological treatment for the reduction of organics typically follows either chemical or physical treatment.

Non-hazardous waste can be treated onsite using one of these methods, but ultimately they must be disposed of at a treatment facility or municipal sanitary sewer system (with permission).

DISPOSAL

Even though biobased MWFs are biodegradable, because of additives, dissolved metals and other contaminants, there are still disposal issues. The decision to dispose is usually based on either time in use, loss of key properties or contamination (including biological contaminants) that exceeds a prescribed limit.

For operations that generate a relatively small amount of MWF wastewater, contract hauling or evaporation probably are the best disposal methods from cost and practicality perspectives.

Before disposal, facilities with spent MWFs need to determine whether the MWFs are hazardous. A substance is considered hazardous by the EPA if it contains any hazardous material. However, metal cuttings removed from MWFs are exempt from hazardous waste disposal requirements and can be recycled.

In the case of an inadvertent release into the environment with no intervention, straight mineral oil biodegrades anywhere from 15-35 percent, and straight vegetable oil biodegrades 70-100 percent.

Best Practices For Maintaining Coolant Quality[5]

Coolants need to be filtered and recycled regularly and the equipment completely cleaned at least annually. Assuming that workers are continuously removing metal chips and tramp oil, the Ohio EPA recommends the following coolant system cleaning practices for maintaining optimal fluid quality:

- Remove the coolant.
- Remove all metal chips and fines.
- Clean any oily residues that remain on any surface.
- Fill the sump with a good cleaner using clean water and circulate the cleaner through the coolant system for several hours.
- Apply cleaning solution to the machine surfaces that are not contacted by the coolant during machine operation.
- Pump cleaning solution from the sump.
- Wipe cleaning solution residues from the sump.
- Rinse the entire coolant system with clean water. Wipe off cleaned surfaces that are not contacted by the rinse water cycling through the system. Rinse the system again if necessary to remove all residues.
- Recharge the system with reclaimed or new coolant immediately to protect metal surfaces against corrosion.

[5] From: **http://www.epa.ohio.gov/ocapp/p2/fact11.aspx.**

SUMMARY

What would seem to be a relatively small expenditure for most companies can have a big impact on the bottom line. Researchers estimate that MWFs comprise less than 5 percent of total plant expenditures yet can impact more than 40 percent of the plant's operational budget.

Honary doesn't consider biobased MWFs to be a novelty anymore, pointing out that The UNI-NABL Center licensed several biobased MWFs and coolants for commercial use in 2000, and the products are currently in the market performing successfully.

Mott also sees mostly blue skies for biobased MWFs. "The industry is moving to green fluids to better comply with OSHA standards and improve on best practices," he says. "Vegetable-based fluids offer improved worker safety and health benefits as well as economics in terms of tool life. From a right-thing-to-do viewpoint, I also believe individuals and companies want to go green when they can because it just makes sense to do so. It is much more a part of the discussion today than it was 10 years ago. I see continued growth for vegetable oils. Year-over-year sales for vegetable-based oils used as basestocks have been a good area of incremental growth in our industry."

Experts agree that with additives being roughly equal, there is a definite environmental advantage to going green. TLT

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[4] "Metalworking Fluids—Clearing Away the Mist?" *ANN OCCUP HYG*, (2005), **49**(4), pp. 279-281. **http://annhyg.oxfordjournals.org/content/49/4/283.full.**

Milind Phadke

Analysis: The global metalworking fluids market

KEY CONCEPTS

- Demand for metalworking fluids in 2012 is estimated at 2.2 million tons, about the same as 2007.
- Kline & Co. projects moderate growth in the metalworking fluids industry, with 2022 consumption reaching about 2.4 million tons.
- The trend to outsource manufacturing to low-cost Asian nations is winding down and might reverse.

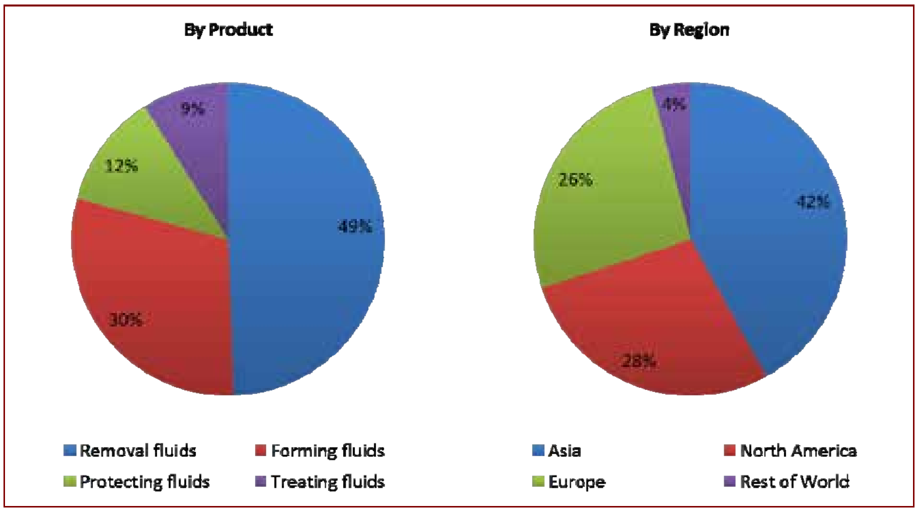
Modest consumption increases are forecasted, accompanied by shifts in production sources.

THE GLOBAL DEMAND FOR METALWORKING FLUIDS in 2012 is estimated at 2.2 million tons. This represents an essentially flat market in comparison to 2007 when demand was estimated at 2.3 million tons.

PRODUCTS

Removal fluids (or coolants) account for almost half of the total metalworking fluid consumption. Forming fluids (which include rolling oils, drawing and stamping fluids) and forging fluids account for 30 percent of the total demand. Protecting fluids account for 12 percent, and treating fluids account for 9 percent.

Besides a functional classification, products also are categorized on the basis of their composition into straight (or neat) oils and water-miscible fluids. Water-miscible fluids can be further classified as soluble oils, semisynthetic fluids and synthetic fluids. Consumption of removal fluids is generally dominated by water-miscible fluids due to their low usage cost, though straight oils dominate consumption in some markets. In contrast, for both protecting and treating fluids, consumption is dominated by straight oils, though there is a shift toward using water-miscible fluids.



SOURCE: *Kline & Co.*

Figure 1 | **Global Metalworking Fluid Consumption by Product and Region, 2012.**

THE GLOBAL MARKETPLACE

Asia is the largest market with about 42 percent of the total demand, followed by North America with 28 percent. Europe, which includes Western Europe, Central and Eastern Europe, Russia and Turkey, accounts for 26 percent of the total. Rest of World (RoW)—which includes South America, Africa and the Middle East—accounts for about 4 percent of total demand.

The top markets in Europe include Russia, Germany, France, Italy and the United Kingdom. These top five markets account for about 72 percent of the demand in the region. Russia is one of the leading steel and aluminium producers in the world and has a substantial automotive industry. Germany is the leading auto manufacturer in Europe and has a sizable share of the European metals production. Russia, Spain and France are other leading auto manufacturers in Europe. The United Kingdom is the fifth largest auto manufacturer in Europe and has a vibrant aerospace and shipbuilding industry. The presence of these industries drives metalworking fluid consumption in these markets.

The key markets in Asia include China, Japan, India, South Korea, Thailand and Taiwan. Together these markets account for about 95 percent of total Asian demand. All of these countries have extensive manufacturing industries covering automotive manufacturing, steel and aluminium rolling mills, forging operations and machinery manufacturing, all of which contribute to metalworking fluids consumption. In North America, nearly 85 percent of the metalworking consumption is accounted for by the United States, with Canada and Mexico accounting for the balance. Brazil and South Africa are the largest markets in RoW.

ADDITIVE DEMAND

The global additive consumption for metalworking fluids accounts for about 575 kilotonnes. The leading additive categories include corrosion inhibitors, emulsifiers, friction modifiers and EP. Together these four additive categories account for more than 80 percent of the metalworking fluid additive demand. Corrosion inhibitors minimize corrosion and rust, so they are most commonly used in protecting fluids but also are found in other fluids. Emulsifiers are needed for formulating water-miscible fluids.

Additive changes are driven primarily by health, safety and environmental (HSE) considerations. The use of low-molecular weight chlorinated paraffin is restricted or outright banned. These have been replaced by mid-chain and long-chain molecules. However, they are not as effective in offering EP protection, hence their loading is higher. Phosphor and sulphur compounds also are being used as substitutes, but they too bring in their own problems of promoting bioactivity and unpleasant odors.

Besides chlorinated paraffins, the use of metals, in general, is being restricted. There is also a reduction in use of secondary amines and formaldehyde releasing biocides. These HSE factors have all been in play for some 10 to 15 years. They are not new. The displacement of undesirable molecules at a global level is rather slow.

The product development practices in Europe, in particular, are mainly focused on developing new technology out of necessity, due to REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) and other regulations. Most of the new product launches in Europe recently are based on the following technologies:

- Boron- and chlorine-free technology
- Amine-free technology
- Boron/amine-free technology
- Cyclic amine technology
- Hazard label-free technology
- Emulsification of Group II and III and GTL base oil
- Fluids with a lower potential to stain
- Vegetable ester-based materials.

All European companies must follow the REACH legislation of the EU, which is applied not to metalworking fluids but to the ingredients used in their production. These ingredients have to be registered in Europe. REACH is more problematic with water-miscible fluids than with neat oil due to the higher number of ingredients in their formulations. REACH also affects metalworking fluid consumers as they have to provide detailed documentation on metalworking fluid-related issues such as types of fluids used, ways of usage, processes where metalworking fluids are used and waste disposal. Other regulations which affect metalworking fluid suppliers and are followed in all EU countries include the biocide directive and Adaptations to Technical Progress (ATPs).

Due to these regulations, the desire for green products, mostly chlorine, boron and formaldehyde-released-agents-free formulations, is increasing in Europe.

SUPPLIERS

The supplier base for metalworking fluids in North America, Europe and Asia is extremely fragmented. Very few companies have more than 10 percent of the overall market in any region. Additionally, the top 10 suppliers account for just about 45-65 percent of the market. Of course, the picture is quite different at a country level where a few suppliers may dominate the market.

This supply structure is to be expected given that the metalworking fluids industry has a very wide range of products that reflect the variety in machining conditions, the material involved, the operating conditions, the performance requirements from the metalworking fluid and other such factors. Because there are no standardized products, there is no significant economy of scale, leading to a fragmented supply base.

Metalworking fluid suppliers fall primarily into three categories: specialty chemical companies, oil companies and distribution companies. Specialty chemical companies have extensive product lines, strong technical capabilities and also offer application-oriented services. These companies are also leading suppliers of chemical management programs. With a few exceptions, they have greater focus on direct sales.

The second category of suppliers is oil companies. These companies are generally commodity oriented and offer a small set of standardized products like straight mineral oils and water-soluble oils that require minimal service support. Their sales are largely through distributors.

The third category is distributors. They have a local presence, a wide range of products other than metalworking fluids and maintain strong ties with end-users. A few of the larger companies offer chemical management programs in collaboration with specialty companies.

Besides the majors, many of the second-tier companies have a presence in different markets, which allows them to follow their customers to a new geography.

HISTORICAL PERSPECTIVE

The global recession has caused considerable upheaval in the metalworking fluids market. Though the 2012 consumption is practically at the 2007 and 2008 consumption level, the market has gone through considerable upswings and downswings, as shown in Figure 2.

Global metalworking fluid consumption showed a gradual increase between 2004 and 2008. After declining by more than 12 percent in 2009 due to the global recession, consumption has grown in fits and starts and was back to 2004 consumption levels in 2012. What is interesting though is the fact that, during the same period, production levels in key end-use industries have increased by a factor of 1.3 to 1.6.

What explains this situation? Improved housekeeping and on-site refining have helped extend fluid change intervals and hold down metalworking fluid consumption, even as production levels continued to increase. Growth in the share of water-miscible fluids and the increase in dilution rates also have helped. Changes in manufacturing technology such as minimum quantity lubrication and near net shape manufacturing have helped dampen metalworking fluid consumption.

OUTLOOK

Based on the ongoing survey of end-users and suppliers, Kline projects moderate growth in the metalworking fluid industry, with consumption reaching about 2.4 million tons by 2022. On the surface, the industry appears to be staid, but a number of interesting trends are in play.

Changes in base fluids. Due to availability issues, use of API Group I is declining, and the use of hydrocracked basestocks is increasing. This change has advantages and disadvantages. Group I fluids have higher solubility. On the other hand, hydrocracked basestocks have a higher viscosity index and lower misting. Besides Group II/III basestocks, vegetable oils are trying to penetrate formulations. These oils have lower oxidation stability and are susceptible to frosting, as well as lower misting and better lubricity.

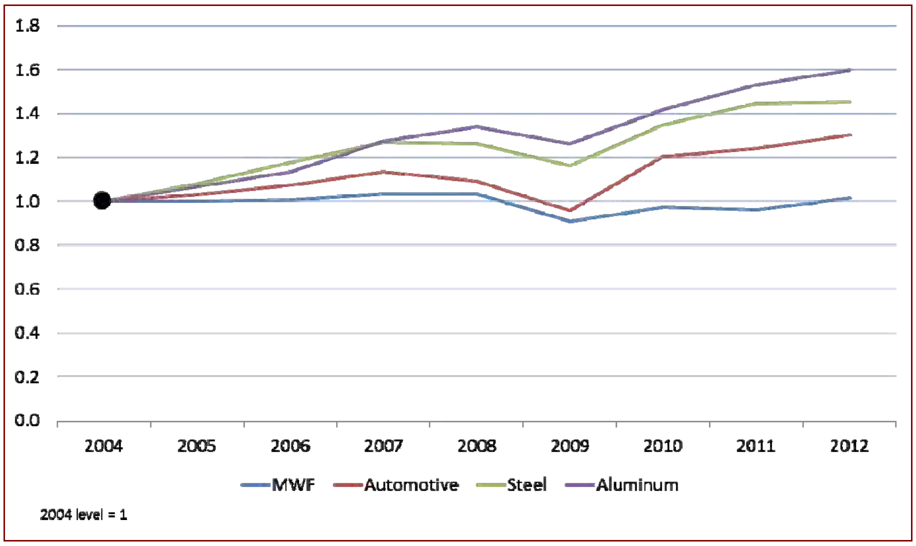
Growth in straight oils. Water-miscible fluids are preferred due to their lower usage cost. Increasing dilution rates offers opportunities to reduce costs. However, there are significant drawbacks. Neat oils are easier to maintain, have a longer tank life and are easier to recycle. In the case of water-miscible fluids, if the cost of effluent testing and treatment is factored in, these fluids can be expensive to use. Additionally, countries such as China and India are experiencing a severe water shortage.

Of the three water-consuming sectors, reducing consumption levels in the household and agriculture sectors by means of higher tariffs is difficult to achieve politically. As a result, industrial users have to bear the brunt of reducing water availability. In many instances, project approvals are tied to the level of water load for the project. Water recycling and usage of straight oils is thus becoming important. Any shift in product preference will be seen mainly for new projects because the cost of the retrofit equipment for using neat oils can be quite high. The recession has made manufacturers conservative, and they do not wish to undertake any projects unless absolutely necessary.

Manufacturing trends. Asia, and in particular China, have benefited from outsourcing the manufacturing from high cost markets in North America and Europe to low-cost destinations. The outsourcing trend is winding down and may reverse altogether.

The recession has created a change in mind sets of rich-world governments. There is an increased desire to protect the manufacturing sector to retain valuable skills and to create jobs. For their part, manufacturers are increasingly concluding that when higher logistics costs, shipping lags and complexity and the threat of intellectual property theft are factored in, it does not make sense to outsource their production. Low-cost Asian countries are increasingly not low-cost due to rising labor costs, lower productivity and, in the case of China, an appreciating currency.

The reversal of outsourced manufacturing will have two effects. First, manufacturing activity in rich countries will stabilize or grow with the corresponding impact on metalworking fluid consumption. Second, low-cost Asian manufacturers will seek to move up the value chain and look to globalize their operations in order to continue growing. This will compel them to modernize their manufacturing processes and pay greater attention to HSE factors. This, in turn, will create an opportunity for higher quality metalworking fluid products, even in low quality markets. TLT



*SOURCE: Kline & Co., **www.oica.net**, World Steel Association and International Aluminium Institute.*

Figure 2 | **Growth in Metalworking Fluid Consumption and Production Levels in Key End-use Industries, 2004 to 2012.**

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Dr. Neil Canter / Contributing Editor

ARE YOU PREPARED FOR GHS?

Lubricant companies should act now to comply with the uniform standard for providing regulatory health and safety information.

KEY CONCEPTS

- The purpose of GHS is to provide a uniform standard for providing health and safety information.
- A new format for safety data sheets and new product labels is required to comply with GHS.
- Due to the complexity of some lubricants such as metalworking fluids, formulators need a strong understanding of the regulation to ensure the transition to GHS is done as smoothly as possible.
- No uniform safety data sheets and labels are achievable because regional differences need to be taken into consideration.
- There is some concern the lubricant industry has not taken steps to comply with GHS, which is to be implemented in the EU and the U.S. on June 1, 2015.

THE MARCH 2013 TLT[1] FEATURED AN ARTICLE ABOUT THE GLOBAL HARMONIZED SYSTEM (GHS) THAT INCLUDED BASIC INFORMATION ON HOW THE LUBRICANT INDUSTRY CAN COMPLY WITH THIS REGULATION, which becomes effective on June 1, 2015. With about six months to go before implementation, there is still concern that the lubricant industry is not moving forward with the steps needed to comply with GHS.

This follow-up article is designed to remind industry players that they now have fewer than six months to comply. If your company has not started to take steps to comply with GHS, there is still time to do so.

Handling regulatory health and safety matters has become an enormous challenge for the lubricant industry. There are matters of preparing safety data sheets (SDSs), product labels and answering questions about specific concerns from end-users.

To make matters even more complicated, different regions of the world have developed different formats and regulations for handling health and safety matters. For example, a SDS in the U.S. is formatted differently than one in Canada and in the European Union (EU).

In addition, each country or region may evaluate a specific chemical substance in a different fashion. An example showing how a specific chemical substance is evaluated by 10 countries and the EU is shown in Figure 1. This unnamed substance has at least four ratings, ranging from non-toxic to toxic.

Also adding to the complexity of the situation is the process that needs to be used for developing SDSs and product labels for lubricants, which are mixtures of various basestocks and additives. In particular, metalworking fluids (MWFs) can be extremely complicated to deal with because they are prepared from a diverse number of additives.

As today's economy has become more global, with lubricant companies shipping products to many different geographical markets, the pressure has increased to develop a uniform format for providing health and safety information on specific chemical substances and on mixtures such as lubricants.

Figure 1 | **This slide from a representative of the European Association of Chemical Distributors shows how one chemical substance is evaluated by 10 countries and the EU. This example helps to justify the need for GHS.** *(Courtesy of C.S.B. GmbH)*

The initial efforts to develop a uniform standard were proposed by the United Nations (UN) in 1992 at the Rio Conference convened by the Organization for Economic Cooperation and Development (OECD). Approval took place in 2002, and the regulation is known as the Global Harmonized System of Classification and Labeling of Chemicals or GHS.[2]

The five main purposes of GHS include:

1. Enhance protection of human health and the environment.
2. Bridge the differences among the systems implemented in the developed world (Canada, EU and U.S.).
3. Develop a framework that can be used by still-developing countries without a system.
4. Reduce the need for testing and evaluation of chemicals.
5. Facilitate international trade.

Some regions of the world have adopted the GHS. Those include the EU, Japan, Malaysia, New Zealand and Singapore. Two of the more important geographical markets are on the verge of implementing GHS. China is scheduled to adopt GHS at the end of 2014, and Brazil plans to do so at the same time as the U.S.

With the world moving toward a uniform standard, the U.S. Government announced in March 2012, through OSHA, that it will adopt GHS by updating the Hazard Communication Standard.[3] The update is known as HazCom 2012, with final implementation to be done by all lubricant suppliers by June 1, 2015.

While the EU has implemented GHS for specific chemical substances, manufacturers of formulated products, including lubricants, will need to implement GHS in the EU also on June 1, 2015.

Canada also is adopting GHS on June 1, 2015, but the nation has yet to announce an implementation schedule.[4]

The implementation of GHS will lead to a change in the format for preparing regulatory information. Information on the health and safety of specific chemical substances and mixtures will change, and new labels will be introduced.

The purpose of this article is to provide an update on GHS and discuss several key issues. However, it is provided for information purposes only and is not intended to provide legal or compliance instructions. GHS is an extremely important and complex issue for those who manufacture, supply or work with chemicals, and STLE members are advised to retain their own in-house or outside experts to guide them through the implementation and compliance process.

This article will examine such issues as:

1. Starting the GHS compliance process at this late date.
2. Should more training be done?
3. What can be done to obtain GHS-compliant information from suppliers as soon as possible?
4. Any indication that OSHA may be willing to extend the June 1, 2015 deadline.
5. Thoughts on using software packages to expedite the process.
6. An update on Canada's implementation of GHS.

A perspective from the EU is also provided, as it has implemented GHS for specific chemical substances but will be implementing GHS for lubricants at the same time as the U.S.

To seek a broad range of opinions, TLT interviewed the following individuals, some of whom contributed to the first article:

- Mike Ogburn, CAP® program development manager, August Mack Environmental, Inc.
- Dave Morrison, HSE specialist, Castrol Industrial North America.
- Heinz Dobbertin, managing director, C.S.B. GmbH.

New GHS Safety Data Sheet (SDS) Format

Current Format (10 sections)

- Ingredients
- Physical data
- Fire and explosion hazard data
- Reactivity data
- Environmental and disposal information
- Health hazard data
- First aid
- Handling precautions
- Additional information
- Transporting information

GHS Format (16 sections)

- Identification
- Hazard(s) identification
- Composition/information on ingredients
- First aid
- Fire fighting measures
- Accidental release measures
- Handling and storage
- Exposure controls/personal protection
- Physical and chemical properties
- Stability and reactivity
- Toxicological information
- Ecological information
- Disposal
- Transporting information
- Regulatory information
- Other

Figure 2 | **The GHS format for SDS is different than what is generally used at the present time. New sections to be included are shown in blue font.** *(Courtesy of Chemical Solutions)*

- Dr. Eugene White, EHS consultant.
- Carl Wainwright, Americas Product Stewardship Advisor, Global Product Integrity Systems, ExxonMobil Fuels, Lubricants & Specialties Marketing Co.
- Dr. John Howell, president, GHS Resources, Inc.

GHS BASICS

The first thing to note in moving to GHS is that the format for the SDS changes. Figure 2 shows the differences between a format commonly used now and the new GHS format. There are 16 sections in the new format as compared to 8-10 sections that are most commonly used at present. Most of the same sections are included, though they are organized in a different fashion. The four new sections are listed in blue font.

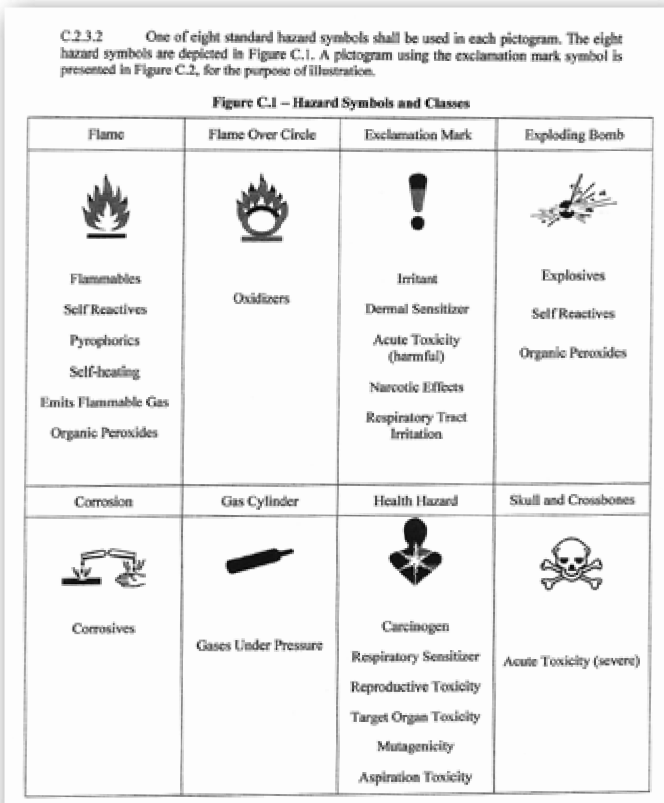
For the SDS, each of the sections must be written in order from Section One (Identification) through Section 16 (Other). But note that the ecological, disposal, transport and regulatory information sections are not required.

Other elements included on the SDS and the product labels are pictograms, signal words, hazard statement and a precautionary statement. Each pictogram represents at least one hazard class. Appendix C of HazCom 2012 provides a full description of these hazard classes and the mandatory language that must be used with them. Figure 3 taken from Appendix C shows the pictograms and the hazard classes covered by each of them. If the specific lubricant is found to meet the guideline for one of the hazard classes, then the pictogram must be used on the SDS and product label. Only the environment pictogram will not be mandatory under GHS.

From the MWF perspective, the most likely pictograms are the exclamation mark and corrosion. Figure 3 shows what it means for a product to have either of these labels. An exclamation mark means that the substance could be an irritant (skin and eyes), skin sensitizer, exhibits acute toxicity and is a respiratory tract irritant. For corrosion, the substance can cause skin corrosion/burns, eye damage and also be corrosive to metals.

The signal words needed to classify a MWF are either *DANGER* or *WARNING*. The former is an indication that the fluid is a severe hazard, while the latter means that it is a less severe hazard. Hazard statements are used to describe the nature and, where appropriate, the degree of the hazard. Precautionary statements are used to recommend ways to minimize or prevent adverse effects.

Each of the hazard classes is further subdivided into several categories that are given a numeric rating. The number of subdivisions is dependent upon the hazard class. In general for GHS, the lowest number (usually one) represents the most hazardous category. This approach is completely opposite to how the Hazard Material Identification System (HMIS®) and the National Fire Protection Association (NFPA) are organized. Both systems, widely used in the U.S., rank the most severe rating with the highest number.



C.2.3.2 One of eight standard hazard symbols shall be used in each pictogram. The eight hazard symbols are depicted in Figure C.1. A pictogram using the exclamation mark symbol is presented in Figure C.2, for the purpose of illustration.

Figure C.1 – Hazard Symbols and Classes

Flame	Flame Over Circle	Exclamation Mark	Exploding Bomb
Flammables Self Reactives Pyrophorics Self-heating Emits Flammable Gas Organic Peroxides	Oxidizers	Irritant Dermal Sensitizer Acute Toxicity (harmful) Narcotic Effects Respiratory Tract Irritation	Explosives Self Reactives Organic Peroxides
Corrosion	**Gas Cylinder**	**Health Hazard**	**Skull and Crossbones**
Corrosives	Gases Under Pressure	Carcinogen Respiratory Sensitizer Reproductive Toxicity Target Organ Toxicity Mutagenicity Aspiration Toxicity	Acute Toxicity (severe)

Figure 3 | **This figure taken directly from Appendix C of HazCom 2012 shows the eight pictograms that will need to be used on SDSs and labels and what hazard classes they cover.** *(Courtesy of GHS Resources, Inc.)*

Estimating Skin Hazards based on known ingredient information

- Table A.2.4 **Concentration of ingredients of a mixture for which the additivity approach does not apply, that would trigger classification of the mixture as hazardous to skin**

Ingredient	Concentration	Mixture classified as skin
Acid with pH < 2	> 1%	Category 1
Base with pH > 11.5	> 1%	Category 1
Other corrosive (Category 1) ingredients for which additivity does not apply	> 1%	Category 1
Other irritant (Category 2) ingredients for which additivity does not apply, including acids and bases	> 3%	Category 2

Figure 4 | **The threshold method is shown as applied to skin hazards. Classification of skin hazards is made based on the pH of the mixture or on whether a specific raw material in Category 1 or 2 is at a concentration where the entire mixture must be designated in either of those categories. The table number refers to its location in Appendix A of HazCom 2012.** *(Courtesy of GHS Resources, Inc.)*

The optimum way to evaluate a lubricant is to use test data. When not available, hazards can be estimated by using either the threshold or additivity method. The former involves determining the concentration of a specific component and comparing it to a specific concentration limit. In the latter, the sum of the concentration of specific ingredients is calculated to see if the value exceeds a specific concentration limit. Requirements for specific categories within hazard classes are provided in Appendix A of the HazCom 2012.

One of the most common issues for MWFs is skin irritation due to the high alkalinity of many water-based fluids. Under the GHS format, the threshold method applies, as shown in Figure 4. Either the pH of the mixture determines its classification as a skin irritant or else the classification of specific Category 1 and 2 raw materials that cannot be evaluated using the additivity approach.

One of the raw materials for which the additivity approach does not apply is acids and bases. As shown in Figure 5, MWF formulators also will need to evaluate the potential salts that can be formed from the variety of bases and acids used. These salts also must be taken into consideration in evaluating the hazardous nature of a MWF formulation.

Guidelines for the additivity method are shown in Figure 6 for the Category 1 and 2 hazard categories. During his presentation on GHS at STLE's 2012 Annual Meeting, STLE Fellow Dr. John Howell, president of GHS Resources, Inc., in Edinboro, Pa., showed how the additivity method is used in Figure 7.[5]

In this example, he evaluated a fictitious MWF containing the following raw materials:

1. Monoethanolamine (MEA) = 0.9 percent (Category 1)
2. Triethanolamine (TEA) = 2.0 percent (Category 2)
3. Sodium Petroleum Sulfonate (Na Pet Sulf) = 4.0 percent (Category 2).

As noted in Figure 7, the process involves first determining if there is sufficient concentration of all Category 1 raw materials for the MWF. The only Category 1 raw material is MEA, which is present at a concentration that does not equal 5 percent.

Then the process moves to evaluation of the two Category 2 raw materials: TEA and sodium petroleum sulfonate. In the calculations, MEA has to be included as a Category 1 raw material, and its presence in the MWF means that the concentration of Category 2 raw materials exceeds the 10 percent

Salt Formation

Bases

- **Monoethanolamine (MEA)**
- **Triethanolamine (TEA)**
- **Sodium Hydroxide**
- **Potassium Hydroxide**

Acids

- **Oleic Acid**
- **Tall Oil Fatty Acid**
- **Caprylic Acid**
- **Neodecanoic Acid**
- **Pelargonic Acid**
- **Boric Acid**
- **C10 – C12 Diacids (sebacic, undecanedioic and dodecanedioic)**

Figure 5 | **Any one of the bases in the left column can form a salt with an acid in the right column in a metalworking fluid. Formulators will need to evaluate potential salts when determining how to properly prepare a GHS SDS and label for their products.** *(Courtesy of Chemical Solutions)* limit. The result is the MWF must be designated as skin Category 2 under the GHS system.

Compliance with GHS is mandatory in the EU and the U.S. by June 1, 2015. All companies involved (manufacturers, distributors and users) may continue to follow the same procedures for preparing SDSs and labels that they currently use and that are in compliance with current regulations until converting over to GHS. U.S. distributors may sell products in compliance with current regulations for six additional months (until Dec. 1, 2015).

Estimating Skin Hazards based on known ingredient information

- Table A.2.3 **Concentration of ingredients of a mixture classified as Skin Category 1 and/or Skin Category 1 or 2 that would trigger classification of the mixtures as hazardous to skin**

	Concentration triggering classification of mixture as	
Sum of ingredients classified as	Skin corrosive Category 1	Skin irritant Category 2
Skin Category 1	≥ 5%	≥ 1% but < 5%
Skin Category 2		≥ 10%
10 x (Skin Category 1) + Skin Category 2		≥ 10%

Figure 6 | **Guidelines for using the additivity method for determining the skin hazard category for a metalworking fluid formulation are shown. Note the final designation involves not just the individual rankings of raw materials but their sum. The table number refers to its location in Appendix A of HazCom 2012.** *(Courtesy of GHS Resources, Inc.)*

Armed with this information, the MWF formulator must now evaluate its product formulations to assess the nature of hazards. MWFs are extremely complex, making this process very difficult.

Typically, preparation of SDSs is carried out in part by reviewing information obtained from raw material suppliers. At this point, raw material suppliers must meet the same timeline as MWF formulators, which mean they do not have to provide GHS SDSs until June 1, 2015.

One source that lubricant formulators should use to evaluate the rating of raw materials is the European Chemicals Agency (ECHA), Classification & Labeling (C&L) Inventory Database that can be accessed at **http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database.**

The information is provided by notifications from all companies using a particular chemical substance in the EU. Ratings for specific chemical substances can vary, and the ECHA does not make any recommendations about what rating to use nor does it verify the accuracy of the information uploaded into the database. In addition, the inventory is constantly updated, so any users should frequently check back to see what if any new data has been inputted into the database.

HOW TO GET STARTED

Rest assured that compliance with GHS must be done. STLE member Dr. Eugene White, environmental, health and safety (EHS) consultant in Cincinnati, Ohio, clearly states that GHS compliance is mandatory. "My major concern at this point is some companies have not yet started the process even though June 1, 2015 is just around the corner," White says. "Though GHS requirements are basically straightforward, they are comprehensive and it takes time to properly modify pre-GHS labels and convert MSDSs to the 16-section standardized SDS format. Whether these document changes are made by in-house EHS staff or outsourced to GHS vendors, becoming GHS compliant is not an optional administrative item subject to laissez-faire consideration. Companies do not get a pass for trying to be regulatory compliant—either you are compliant or you are not!"

Suppose that your company has not started to comply with GHS. What three steps can you take to get started?

Howell focuses on determining resources needed, checking on label printer capabilities and focusing on a lubricant manufacturer's top-selling products. He says, "Right away, begin to identify the resources required to do the job. Beginning this late in the game will require hiring new environmental, health and safety (EH&S) resources, diverting additional human resources to this effort or reassignments of other job responsibilities. Second, consider whether you will need to purchase or lease SDS software or hire a third-party contractor who has such software to prepare your SDSs. Third, after reading and thoroughly understanding 29 CFR 1910.1200, Appendix A, hand-classify the top 20 percent of products, which likely produce some 80 percent of your sales. That way, you can begin to understand the changes in labels and SDSs your customers will shortly be seeing."

Carl Wainwright, Americas Product Stewardship Advisor, Global Product Integrity Systems for ExxonMobil Fuels, Lubricants & Specialties Marketing Co. in Paulsboro, N.J., suggests a systematic approach where information is first obtained on component ingredients, followed by analysis and implementation. He says, "In order to ensure that their GHS compliance activities are on track, a lubricant manufacturer would need to first obtain the GHS hazard classifications and SDSs for each of their component ingredients from each of their suppliers. The lubricant manufacturer will then need to assess the information received and determine the appropriate GHS classification and labeling requirements for their finished lubricant products. Finally, the lubricant manufacturer would need to implement a plan to update their SDS and product labeling, as well as working down inventory to minimize relabeling, if needed."

Mike Ogburn, eCAP® program development manager for Indianapolis-based August Mack Environmental, Inc., reminds companies that training needed to be done last year but still is important in getting started with GHS. He says, "Dec. 1, 2013, was the effective completion compliance deadline for training employees on the new label elements and the revised SDSs. This must still be done first because without the training, the pictograms and hazard statements will mean very little to someone on the production floor."

Ogburn then suggests, if possible, that a base product be identified by the lubricant company as a basis for assigning appropriate hazard classifications. Finally, he says, "Establish constant communication with your suppliers and then dedicate within your company the resources needed to accomplish this task."

CHALLENGES

No matter how much progress your company has made to date, there are still a number of challenges that will need to be dealt with along the way.

Supplier information. One of the most important issues is how to access information on components used in your products. This can be a particular challenge, especially for MWF companies that manufacture 100s of products, each of which may contain 20 substances.

Wainwright states that securing substance information for suppliers is a difficult process. He says, "OSHA has adopted a single-phase approach for substance and mixture GHS implementation, so substance manufacturers and finished lubricant manufacturers will have the same implementation deadline of June 1, 2015. This means that not all GHS information from substance suppliers may be readily available for lubricant manufacturers to assess in their own products in a timely fashion."

In addressing how to persuade suppliers to share GHS-compliant labels and SDSs on their substances, Wainwright suggests developing a close relationship with suppliers and look for information from other sources.

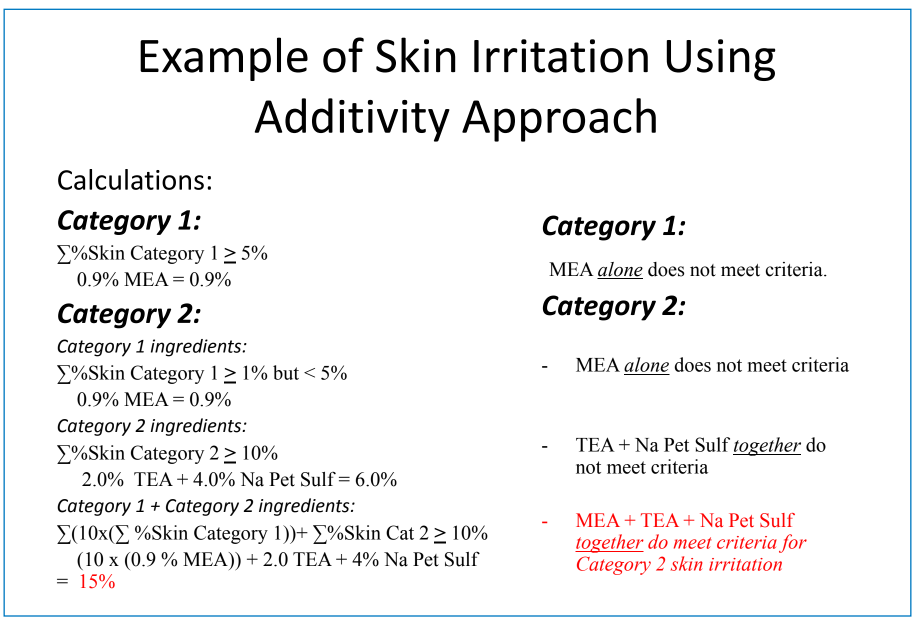


Figure 7 | **The process for using the additivity method to determine the skin hazard category for a metalworking fluid containing specific concentrations of MEA, TEA and sodium petroleum sulfonate is shown.** *(Courtesy of GHS Resources, Inc.)*

He says, "Try to work directly with your supplier's product safety departments. Most suppliers should have access to GHS hazard classifications of their products at this point. Send written requests to your suppliers and keep copies of these requests for documentation purposes."

Other sources include the EU C&L Inventory Database discussed earlier in this article. Wainwright continues, "You can also consider the use of GHS SDSs from other countries or suppliers to see how others are classifying a given substance. The main risk to this is when your supplier does provide the GHS information for their product. You might need to update your SDS and labels if there are discrepancies or additional information."

Ogburn suggests that an attempt should be made to use leverage with your supplier to facilitate receiving GHS compliant information in a timely manner. He says, "If you have a good relationship with your supplier (which usually means you are purchasing a lot from them), then you have some leverage. No company wants to lose a good customer. So if you are important to your suppliers, they should be able to get you the data you need."

Howell believes that applying pressure on suppliers is essential and all efforts should be documented. He says, "Lubricant manufacturers need to pressure their suppliers by any suitable means to get GHS-compliant SDSs into their hands, sooner rather than later. No matter which steps you take, writing letters, emails, phone calls, etc., document your efforts, as those documented steps may become important later."

Suitable hardware and software. GHS-compliant SDSs and labels will need to be bicolor so that a black pictogram can be printed with a red diamond. Howell says, "SDSs software is virtually essential unless you have a small product line and market only within the U.S. In assessing your capabilities, review the label printers you have available to confirm that you can print red-bordered pictograms or can overprint preprinted, blank and red-bordered pictograms with black ink."

Wainwright adds, "You may need to invest in new printers or start to purchase preprinted label stock. Alternatively, you can source your SDSs and labels from a third-party vendor."

On the matter of software packages, Howell believes that they are nearly essential if the manufacturer is marketing products internationally. He says, "Software packages certainly can assist a lubricant manufacturer if it markets in jurisdictions where other languages besides English are required or detailed. While OSHA had promised a Word template, which would be useful for such producers, indications are that such a template may not be ready for some time due to resource constraints at the agency."

Caution is essential if you decide to purchase a GHS software package. Howell says, "If manufacturers have not used such software before, they should expect to spend a significant amount of time in training and how to effectively use the software."

Ogburn provides his perspective on software packages. He says, "What we are hearing on the street is that software packages are expensive and the integration is complex. Most software packages are using a rule-based system to automatically generate hazard classes and statements and then placing the correct pictogram on the SDS. To date, 90 percent of our clients that deal with software packages have been disappointed with the results and have faced significant cost overruns."

Heinz Dobbertin, managing director for C.S.B. GmbH in Krefeld, Germany, believes that preparation of SDSs and labels cannot be done without the correct software. He says, "People should be very careful about which software is chosen and be particularly cautious as to the process used to update SDSs and labels is handled."

Relabeling. Once you feel that you have developed SDSs and labels for all of your products, do not forget about existing inventory that has not been sold by June 1, 2015. Wainwright says, "Another important hurdle that needs to be addressed is relabeling finished product already packaged at your facility that does not meet GHS requirements. Relabeling or repackaging could be quite labor intensive and costly. Manufacturers and distributors will need to weigh these costs versus writing off existing inventory that does not have GHS-compliant labels."

The implementation of GHS will lead to a change in the format for preparing regulatory information.

EMPLOYEE TRAINING

Training was covered as an important issue in the March 2013 TLT article, which was written before OSHA's required deadline for training on Dec. 1, 2013. Since training has been accomplished, the question is asked about whether it is important to continue training.

STLE member Dave Morrison, HSE specialist for Castrol Industrial North America in Naperville, Ill., said in the March 2013 TLT article that the timing between GHS implementation and training was too long. He says, "This issue remains a concern for us. As an experience trainer, there are many instances where I ask a class a question regarding recent training that I know they have had. At least half the class cannot remember taking it. So I know based upon that experience that employees looking at SDSs will not remember their OSHA training. Even so, many parts of the SDS are self-explanatory. However, even with the OSHA training there may be parts of the SDS that require the interpretation of a safety professional."

All of those interviewed agree that repeat training is essential. White says, "It does not hurt to provide refresher education to reinforce prior knowledge and clarify key learning elements. OSHA provides user-friendly GHS educational materials with explanations of labels, pictograms, SDS sections, signal words, hazard statements and precautionary statements."

Howell adds, "Just as important, lubricant manufacturers should assist their customers with their training responsibilities by sharing with them new lubricant product labels and SDSs before they are formally published. That way, you can work with your key customers and address any concerns that they might have about your product labels and SDSs before they actually arrive on the customer's shipping dock and are placed in the supply room."

Ogburn advises that continuing training is a must because at last one very important concept is still not understood. He says, "Right now having employees differentiate between the signal words *DANGER* and *WARNING* seems to be a sticking point. Do your employees know and fully understand the difference between these two terms?"

Wainwright says, "OSHA Hazard Communication training needs to be done for all new employees who handle hazardous substances, and it is beneficial to include GHS refresher training for employees before/during your company's GHS implementation."

MWF PERSPECTIVE

With the complexity of most MWFs, there are additional issues that need to be dealt with due to the large number and different types of chemical substances used.

Morrison says, "Currently, customers are asking for updated SDSs just to be in compliance, without regard to what has or may have changed. Even so, not many SDSs have been released to the metalworking fluid end-user yet. When they do start to flow, it will take some time for people to realize that some of the warnings have changed. In the early stages, companies are just collecting SDSs and not likely examining them for changes."

In reviewing the large number of additives, the question was asked about which key raw material types may be more difficult for the MWF suppliers to deal with in developing GHS-compliant SDSs and labels. White says, "I stand by my comments from the initial article that corrosive chemicals and biocides are the two raw material categories that should be scrutinized carefully. Both of these additive types can have acute health effects if not utilized properly. Metalworking fluid suppliers will need to use GHS guidelines for SDSs and labels to provide adequate information to end-users."

Morrison feels that those components such as salts that are formed as the fluid is prepared warrant attention. He says, "Those formulations with salts or other reaction products whose base components have greater health concerns than their reaction products need to be carefully evaluated because there is limited to no information on some of these substances."

Morrison continues by expressing what needs to be done to gain a better understanding of these substances. He says, "Testing salts and reaction products is the only answer if we wish to continue using them. The cost involved in testing may limit the number of options available to the metalworking fluid formulator in the future."

White sees communication between raw material suppliers and MWF manufacturers as critical in gaining a better understanding of how to work with corrosive chemicals and biocides. "Accurate information on these substances can be provided only if raw material suppliers and metalworking fluid manufacturers have a good relationship. Through educational activities that some suppliers offer and through the efforts of organizations such as ILMA and STLE, much valuable information about product components is disseminated throughout the industry," White says. "For matters of confidential information on certain raw materials, GHS has instituted guidelines to help both raw material suppliers and metalworking fluid manufacturers."

Howell details the changes in how trade secrecy is dealt with under GHS. "There have been no changes in the trade secret provisions between HazCom 1994 and HazCom 2012 as described in Appendix E. What has changed is the default requirement of what should be disclosed in Section 3 of the SDS," Howell says. "Previously, manufacturers needed to disclose just those components that have an OSHA Permissible Exposure Limit (PEL), an ACGIH Threshold Limit Value (TLV), those which appear on one of several lists of carcinogens or other chemical lists, which contributed to the product's hazards. Under HazCom 2012 *(see Appendix D, Table D.1)* manufacturers must list, for mixtures, the chemical name, common names and synonyms, CAS number and other unique identifiers, the exact concentration of all ingredients, which are themselves classified as health hazards and which are present above their concentration/cut-off limits or which present a health risk below the cut-off/concentration limit. When a trade secret is claimed in accordance with paragraph (i) of 29 CFR 1910.1200, a statement that the specific chemical identity and or exact percentage (concentration) of composition has been withheld as a trade secret is required."

Howell continues, "Manufacturers should understand that the trade secret provisions are different in the United States than in other jurisdictions and that either registration of the trade secret with a competent authority or more disclosure elsewhere may be required."

Ogburn believes that providing reasons for claiming trade secrecy must be clearly documented. He says, "The best course of action is to fully document how and why disclosing trade secrecy information on the SDS will harm business interest."

With uncertainty about certain chemical substances, this raises the issue of whether it will be necessary to reformulate products. Morrison says, "At this time, there is very little to no pressure on metalworking fluid manufacturers to reformulate. In actuality, the pressure to change the composition of a fluid will be indirect because the SDSs will determine if a fluid will sell in the marketplace. If the fluid fails due to its SDS, then the manufacturer will be faced with the decision to do testing (if it promises to improve the product's rating), reformulate or discontinue the product."

White says, "The metalworking fluid industry as a whole has been proactive over the years in modifying the chemistries of certain products in response to compelling data from health and safety research sources. At this time, manufacturers may be compelled to reformulate, if necessary."

Howell sees reformulation efforts as being underway but limited. He stresses the value of testing the eye and skin irritation of specific MWFs. "Metalworking fluid manufacturers are finding that products marketed as "mild to the hands" are, in fact, classified, according to the criteria in Appendix A, as a Category 1 eye corrosive and perhaps as a Category 1 skin corrosive," Howell says. "In truth, the products may not possess the corrosive hazards that are listed in the Appendix A classifications. In those cases, actual product testing for eye and skin irritation can be an alternative to reformulation and, in the long run, costly. But remember that actual testing data, if available, must be used in place of the procedures described in Appendix A."

With the complexity of most metalworking fluids, there are additional issues that need to be dealt with due to the large number and different types of chemical substances used.

DELAYING THE GHS DEADLINE

The concern with not having adequate information from raw material suppliers is prompting efforts by the lubricant industry to persuade OSHA to delay GHS implementation. Wainwright says, "ILMA has recently petitioned OSHA because of delays in receiving raw material information from suppliers. While it can be difficult to predict the outcome of these efforts, it is unlikely that OSHA will be willing to make changes so close to the implementation deadline. Although U.S. GHS implementation is being done in a single phase for substances and mixtures, OSHA may take the view that industry has had more than three years to prepare."

With no assurance there will be a delay in GHS implementation, Howell reveals that ILMA has asked for more support from OSHA. He says, "ILMA has suggested that for those lubricant manufacturers who are making good-faith efforts to classify products and prepare GHS-complaint SDSs and labels that if the SDS and labels for certain products for which upstream component SDSs have not been received in a timely manner, that OSHA not cite such manufactures for not having all of those finished product SDSs complete if an inspection were to occur after June 1, 2015. ILMA has suggested a six-month window to complete those finished product SDSs and labels."

Howell indicated that not only ILMA but the American Coating Association, in a letter co-signed by eight other associations, also has petitioned OSHA seeking temporary relief from the deadline.

In a late breaking development, OSHA has responded to the American Coating Association after a meeting with this organization and ILMA last October. Howell says, "OSHA did not agree to extend the deadline for implementation of GHS in the U.S."

Howell shared the following information from a letter that Dr. David Michaels, assistant secretary of labor for occupational health and safety, wrote in response to J. Andrew Doyle, president of the American Coating Association.

Howell indicated that Dr. Michaels wrote, "OSHA is able to use its enforcement discretion when the compliance staff consider whether formulators and manufacturers have performed their due diligence and made good faith efforts to obtain necessary information to comply with the June 1, 2015 deadline. Manufacturers and formulators should therefore document all efforts to alternatively obtain the required information; such as attempts to contact their supplier to obtain the proper information; reasonable efforts to find alternate suppliers who could provide timely and accurate classification; and reasonable efforts to find relevant data themselves."

EU PERSPECTIVE

Dobbertin comments on the continuing challenge to complying with GHS, not just in the EU but in other parts of the world. He says, "Classification of many substances are different in the various countries, labeling is handled differently and which modules of GHS have been implemented is also different. This leads to the fact that in each country, the responsible party for first introduction of a substance/mixture/product has to check if the country of their supplier is using the same modules and if there are different classifications for the substance."

Dobbertin points out that the need to follow this step is in direct contradiction to the objective of GHS.

At this time in the EU, raw material suppliers have issued SDSs with the CLP classification. The challenge then is to accurately prepare SDSs for lubricants and other mixtures, which is also due on June 1, 2015.

Dobbertin says, "The SDSs prepared by raw material suppliers now show more severe elements (especially in the field of irritation/corrosion), and that needs a lot of explanation as their customers do not understand why the same product all of a sudden shows the corrosion symbol instead of an irritation symbol."

Dobbertin predicts that as the June 1, 2015 deadline approaches, lubricant manufacturers in the EU will face a very similar problem to lubricant manufacturers in the U.S.

Another issue that anyone doing business in the EU must be aware of is how to not just be in compliance with GHS but also with REACH. Details on REACH were provided in a previous TLT article.[6]

Dobbertin sees two issues that need to be overcome as lubricant suppliers need to comply with GHS but also remain in compliance with REACH. "Problems can occur when individual registration dossiers are filed for REACH that contain different GHS classifications for the same chemical substance," he says. "The EU has also asked for extended SDSs, which differ from SDSs, in that they contain at least one exposure scenario for a chemical substance or a mixture such as a lubricant during its operating life. Transferring information from one extended SDS to another is extremely time consuming, as the process can take as long as 18 hours for one SDS. There needs to be a way to make the process more efficient."

Finally, Dobbertin points out that the last tonnage band (1-10 metric tons) for REACH registration is coming up at the end of May 2018. He says, "Discussions are going on to increase the requirements for this registration, which will increase the cost, and there is a strong possibility that the EU will require polymers to be included in registrations in the near future."

Dobbertin cautions that companies will need to decide whether to register chemical substances by the middle of 2016 because there will be an increase in demand to register approximately 20,000 to 25,000 substances from that time until the deadline. Undoubtedly, delays will occur in the registration system, leading to the possibility that a supplier might not be able to register a substance in time and, therefore, be unable to continue to market it to the EU."

RESOURCES

Two resources to use through the process of complying with GHS are the Hazard Communication section of the OSHA Website (**http://www.osha.gov/dsg/hazcom/index.html**) and the European Chemicals Agency (ECHA), Classification & Labeling (C&L) Inventory Database (**http://echa.europa.eu/information-on-chemicals**).

Howell says, "Remember to continue to try to obtain GHS-compliant SDSs from your upstream suppliers. It is imperative that lubricant manufacturers document their requests for GHS-compliant SDSs. Become familiar with the ECHA C&L database, as that can serve as an alternative source for component classification information."

Time is running short as there are fewer than six months to go until GHS is implemented in the EU and the U.S. for lubricants.

Please use all the resources listed plus the suggestions outlined by those interviewed in this article. While this may not ensure that the transition will go smoothly, you will be equipped with the needed information to make it happen.

Good luck! TLT

Neil Canter heads his own consulting company, Chemical Solutions, in Willow Grove, Pa. You can reach him at ***neilcanter@comcast.net.***

REFERENCES

1. Canter, N. (2013), "GHS: New challenges for the lubricant & metalworking fluids industries," TLT, **69** (3), pp 30-39.

2. The UN Regulation can be found at **http://www.unece.org/trans/danger/publi/ghs/ghs_rev01/01files_e.html.**

3. HazCom2012 can be found at **http://www.osha.gov/dsg/hazcom/index.html.**

4. More information on when GHS will become law and implemented in Canada can be found at **http://www.ccohs.ca/oshanswers/chemicals/ghs.html#_1_11.**

5. Howell, J. and Kraska, R. (2012), "2012 OSHA HCS – A close look at trade secrets, hazard classification and using the EU C&L data," Presented at the STLE 2012 Annual Meeting, St. Louis, Mo., May 6-10.

6. Canter, N. (2007), "REACH: The time to act is now!" TLT, **63** (9), pp. 30-39.

20 MINUTES WITH...

Richard Butler

By Karl M. Phipps / Managing Editor

This Certified Metalworking Fluids Specialist explains the role of MWFs and spectroscopic instrumentation used in the condition monitoring of fluids.

Richard Butler
The Quick File:

Work Experience

Rick Butler has more than 30 years in the industrial lubricants business. Currently he serves as technical manager for metalworking at Chemtool Inc., in Rockton, Ill. (outside of Chicago). He has worked primarily as a formulator of metalworking coolants and stamping lubricants throughout most of his career. His technical interests are rust preventive coatings, cleaners, gear oils, liquid gaskets, die-cast release agents, quenchants and biobased lubricants.

Previously, Rick worked as an analytical chemist for Fuchs Lubricants with an interest in developing analytical methods for infrared microscopy and chemometrics, X-ray fluorescence and UV-visible spectroscopy, GC/MS and HPLC chromatography. In addition, he held positions as a facility manager for the North American Chemical Co. in Dallas and Newridge Chemical in Bedford Park, Ill., and Pillsbury Chemical and Oil. He's the father of two college students and enjoys racing sailboats and mountain bicycling.

Education

Bachelor's of Science, Chemistry – Michigan State University, East Lansing, Mich., 1981

Industry Affiliations and Professional Achievements

- STLE member (since 1983)
- STLE Certified Metalworking Fluids Specialist
- Chair, STLE Metalworking Fluids Technical Committee (2011-2012)
- Vice Chair, STLE Condition Monitoring Technical Committee (2011-2012)
- STLE Metalworking Fluids Education Committee
- Member, STLE Chicago and Central Illinois Local Sections (has also presented several technical presentations at the local and national levels)
- Member, Chicago Chromatography Discussion Group, 1995-2005
- President, Society of Applied Spectroscopy (Chicago Section), 2000-2003
- Member, MCM-MSDG (Madison-Chicago-Milwaukee – Mass Spectrometry Discussion Group), 1996-2001

TLT: Why did you choose to work in the lubricants industry?

Butler: After graduating from Michigan State, I was interested in working in the automotive industry in the Detroit area. I wanted to combine my education in chemistry with practical experiences in the engineering field. My first job at Pillsbury Chemical and Oil got me hooked. Soon after starting, I was involved in major troubleshooting calls at both transmission and automobile stamping plants. I soon realized that this could be an interesting career that has an endless variety of challenges without becoming routine and boring.

TLT: What mentors have had the most influence on your career?

Butler: My mentor at Pillsbury was Harris Vahle, who never shrunk away from problems and was interested in teaching young people about the lubricants business. Harris always encouraged me to keep at it and never give up until you solved the problem. Most industrial lubrication problems really boil down to communication difficulties between engineers and chemists.

Other mentors I encountered were Barry Twomey and Steve Hogenboom of D.A. Stuart, who both demonstrated professional lubricant development techniques and shortcuts. However, Chemtool's longtime owner Jim Athans and his family's work ethic is a model that I wish to emulate, as well as Chris Sdregas, Chemtool's vice president of technology, who has great people skills in handling difficult business problems.

TLT: You have expertise in condition monitoring techniques for lubricants. How has condition monitoring of fluids evolved during your career?

Butler: Thirty years ago most analysis was done with wet chemical methods or non-computerized analog instrumentation. The wet chemistry methods were very slow and not all that accurate. Searching infrared spectra qualitatively was done by hand by comparing a strip chart graph against a large Sattler infrared library book. The whole process was so slow it was not really practical. Infrared quantization was difficult and rarely performed.

Starting in the late 1980s, digital instruments became common and practical due to the low cost of personal computers. The advantages of using digital computers for qualitative-library spectral searching and also for facilitating chemometrics quantization of mixtures are now practical and relatively easy.

Gas chromatography with mass spectral detection (GCMS) is now common in MWF analysis. However, liquid chromatography is still under utilized in MWF lubricant analysis.

Most new condition monitoring sensors and programs are geared toward oil analyses of motor oils, gear oils and hydraulic oils. These advances do not apply to or help MWFs. For water-based MWFs, the only specific advances have been in microbiological growth detection. In addition, there have been improvements in the speed and selectivity of microbiological-growth monitoring instruments.

Liquid chromatography with mass spectral detection (LCMS) is the dominant analytical technique for pharmaceutical research.

TLT: Can more sophisticated chromatography and spectroscopy techniques play a role? Are they affordable?

Butler: Liquid chromatography with mass spectral detection (LCMS) is the dominant analytical technique for pharmaceutical research. Lubricant analysis problems are just as difficult as pharmacokinetics problems. LCMS could be a great tool for better understanding the dynamics of degradation within an in-use MWF.

Small handheld slab waveguide infrared spectrometers are affordable and seem to be real instruments. Palm-sized dispersive Raman spectrophotometers are low cost and utilize fiber optic probes. These Raman spectrophotometers can supply almost as much molecular qualitative information as bench-top infrared instruments. Raman has an advantage over infrared as water does not interfere with Raman vibrations.

Soon portable GCMS will be practical. X-ray florescence for elemental analysis is moving away from low resolution and imprecise proportional counter detectors to high resolution, energy dispersive solid-state detection (EDXRF). I would like to see wider use of very high resolution, wavelength dispersive X-ray instruments (WDXRF) as even high resolution EDXRF can be improved.

TLT: What are the challenges of designing modern MWFs?

Butler: Thirty years ago soluble oils were only expected to last two to four months. Now MWF coolants are expected to last a year or longer. Soluble oils do not have good sump life and have lost market share. Users of metalworking coolants do not expect to have to add emulsifiers, defoamers, pH boosters or biocides to help maintain MWF.

Synthetics at 10 percent or above can last up to two to four years as long as the concentration is maintained. However, synthetic MWFs cannot machine all materials in operations. Straight oils are being replaced by water-based MWFs. Semisynthetics are the dominate form of MWF now. Improving the emulsion life of semisynthetics is the main challenge. Novel forms of emulsification hold promise.

TLT: What emerging synthetic lubricant technologies could have a future impact in the industry?

Butler: The only true new synthetic lubrication basestock in the last 30 years is the recent introduction of oil-soluble polyalkylene glycols (OSP). OSPs do not form varnish and hold great promise for automotive gear oils. They have high-heat capacities and thermal transfer abilities to keep truck and race car transmissions and differentials from requiring oil coolers.

TLT: Are there recent industry innovations that will provide a game-changing performance for lubricant formulators?

Butler: The new OSPs have a very low aniline point, meaning high solvency. Like naphthenic oils, they can hold a lot of polar emulsifiers or additives. Blends of OSP and mineral oils have superior varnish resistance compared to other synthetics and Group III basestocks.

For turbine oils, OSPs can solve the varnish problem. The same applies to heat transfer fluids and other high temperature lubricants. They also seem to have inherent lubrication abilities, allowing for reduced additives.

TLT: How important are synthetic MWFs in the industry and are there particular types of synthetics you would prefer?

Butler: Due to long sump life potential, I wish more machining could be done with conventional water-soluble polyalkylene glycols (PAG)-based MWF. Emulsions of OSPs have the potential for long sump life just like water-based PAG. These emulsions are also good as cleaners and have decent rust protection.

TLT: What are the greatest gaps in the product offerings from synthetic PAO, ester and PAG base fluid suppliers and how are they being addressed?

Butler: They are all very expensive. PAO are superior at cold temperature applications but offer no inherent lubricant advantages. Esters are superior lubricants and have high flash points but suffer from poor oxidation resistance. OSP do offer inherent lubrication and non-varnish, high-heat capabilities to help justify the cost increase over conventional mineral oils.

Thirty years ago, soluble oils were only expected to last two to four months. Now MWF coolants are expected to last one year or longer.

TLT: What do you enjoy the most about STLE?

Butler: I was previously a member of the Chicago Chromatography Discussion Group (CCDG) and the Madison-Chicago-Milwaukee Mass Spectroscopy Discussion Group (MCM-MSDG). Both societies failed and dissolved about eight years ago. Unlike STLE, the local sections of these two societies did not have a hierarchy of volunteer subcommittee activity. Also, there was no formal mechanism to move up within the local section subcommittees to become the local or national section chairperson.

The volunteer opportunities to serve in a progression of roles at both the local and national level is STLE's greatest organizational strength. The expectation that STLE volunteers can move up within the organization's hierarchy is unique. In addition, STLE covers a diversity of topics, and the society's technical sections are unrivaled. Finally, STLE's educational and professional certification programs keep getting better each year.

TLT: What advice would you offer to students interested in pursuing a career in lubricant development or tribology research?

Butler: The problems are interesting, varied and endless. Real improvements are still to be gained in lubricant life and performance. Moving away from mineral oil to synthetic basestocks should be the challenge of the next generation.

The ability to speak like an engineer and think like a chemist is invaluable. Taking analytical work courses in advanced mathematics (linear algebra) and partial differential equations will help students solve future complex chemometrics techniques. Meanwhile, learning how to write programs can also be very valuable. Personally, I wish I had taken courses in both microbiology and biochemistry. TLT

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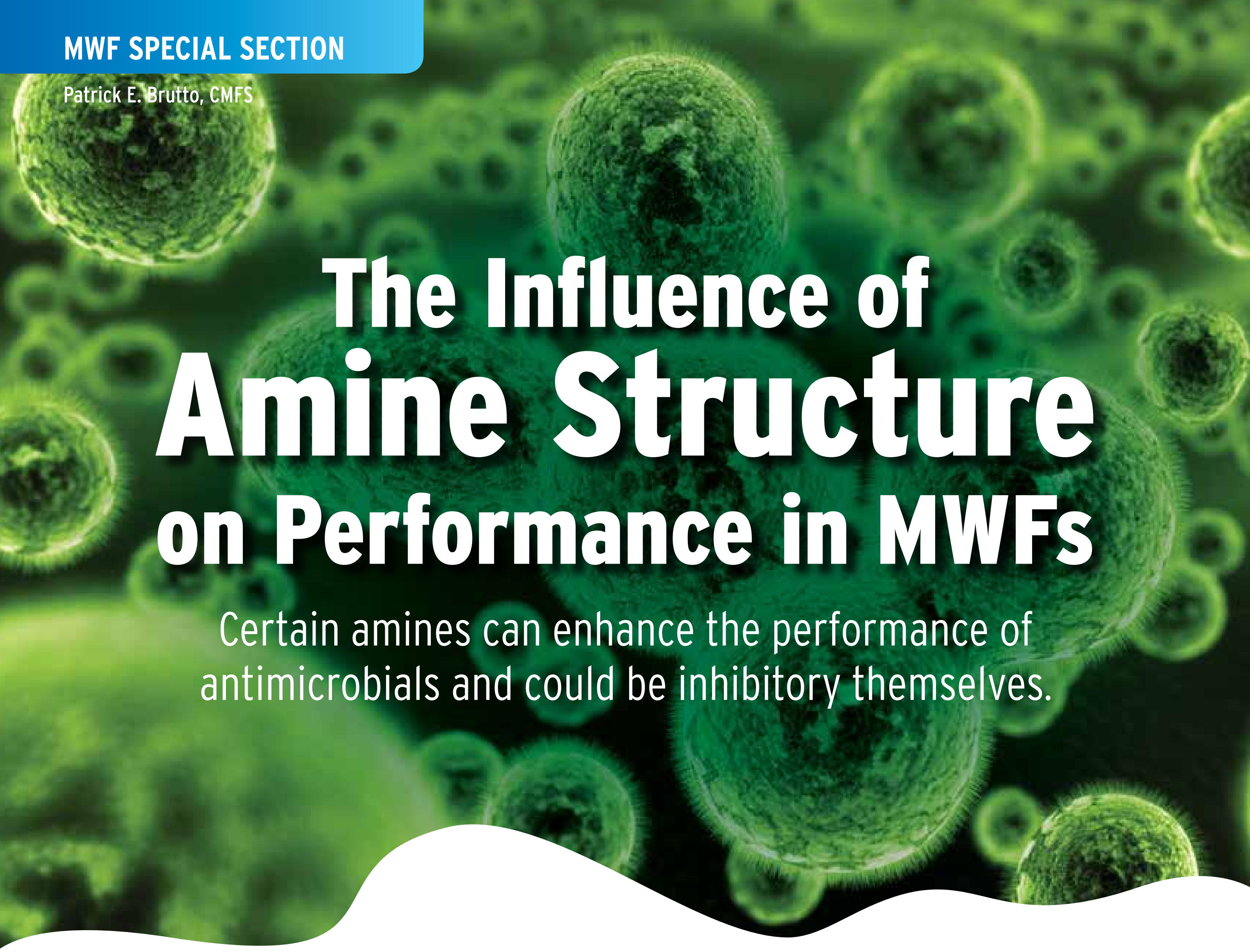

Patrick E. Brutto, CMFS

The Influence of Amine Structure on Performance in MWFs

Certain amines can enhance the performance of antimicrobials and could be inhibitory themselves.

KEY CONCEPTS

- MWFs containing components should theoretically last longer and require less maintenance.
- Several factors can influence the performance of two common biocides: triazine and BIT.
- When all microbiological and corrosion data are considered, the aromatic amine AR-9-1 performs best with BIT.

AMINES AND, IN PARTICULAR, AMINO ALCOHOLS (ALSO CALLED ALKANOLAMINES) HAVE BEEN USED FOR MANY YEARS in water-dilutable metalworking fluids. Their primary functions are (1.) neutralization of acid-functional components and (2.) development and maintenance of alkaline pH. Amine salt/soap reaction products function as emulsifiers, corrosion inhibitors and lubricity agents. In some cases, the unprotonated amines such as triethanolamine provide ferrous metal corrosion control, and some amines such as monoethanolamine are considered bioresistant.[1] This latter property of certain amines or their salt/soap reaction products has become more important in recent years due to the desire for longer-lasting MWFs.

MWFs containing components which resist microbiological attack should theoretically last longer and require less maintenance. Additionally, there are several studies indicating that certain amines can enhance the performance of registered antimicrobials and/or may be inhibitory themselves.[2-6]

What is lacking in the MWF literature is a study of the performance of a wide variety of amine structures of varying carbon number, molecular arrangement and hydroxyl groups, in terms of both microbiological effects with biocides, as well as corrosion control before and during exposure to microorganisms. This article attempts to address this deficiency.

Designation	Chemistry	Status
AL-4-1	2-amino-2-methyl-1-propanol	Commercial
AL-6-1	Butylethanolamine	Commercial
CY-7-1	Proprietary	Experimental
AL-8-1	3-amino-4-octanol	Commercial
AL-8-2	Butyldiethanolamine	Commercial
AL-9-1	Proprietary	Experimental
AR-9-1	Proprietary	Experimental
CY-9-1	Proprietary	Experimental
AL-10-1	Octylethanolamine	Commercial
AL-11-1	Proprietary	Experimental
AL-12-0	Proprietary	Experimental
AL-12-2	Octyldiethanolamine	Commercial
CY-12-0	Dicyclohexylamine	Commercial

Figure 1 | **Amine Compounds**

Ingredient	%
Severely hydrotreated naphthenic oil	10
Sodium petroleum sulfonate	14
Tall oil fatty acid	8
Ethoxylated oxazoline	4
Phosphate ester	2.4
C_{10-12} dicarboxylic acid	2
Nonylphenol ethoxylate (6 mole)	6.4
Propyleneglycol n-butylether	6
Deionized water	Balance to 100%
AMP or potassium hydroxide*	Adjust for pH 9.3-9.7 (at 5% dilution)
Amine (active basis)	6
Biocide	Variable

*AMP: 2-amino-2-methyl-1-propanol

Figure 2 | **MWF Formulation**

AMINE COMPOUNDS

The amine compounds are described in Figure 1. The "Designation" descriptions are as follows: the first two letters indicate molecular structure (AL for aliphatic, CY for cycloaliphatic and AR for aromatic), the middle numbers are the number of carbons and the last number is the number of hydroxyl groups. For example, AL-9-1 is an aliphatic 9-carbon amine with 1-hydroxyl group. As indicated, some of the structures are commercially available, while others are experimental and proprietary.

BIOCIDE COMPOUNDS

The following registered biocides were evaluated in this study:

- Hexahydro-1,3,5-tris(2-hydroxethyl)-s-triazine, supplied as 78 percent active ingredient in water. This biocide will be referred to as "triazine."
- 1,2-Benzisothiazolin-3-one, supplied as 20 percent active in water/dipropylene glycol. This biocide will be referred to as "BIT."

MWF FORMULATION

The following low-oil, boron-free semisynthetic MWF formulation was selected for this study (*see Figure 2*).

MICROBIOLOGY TEST PROTOCOL

Tests were conducted in accordance with ASTM Practice E2275. MWF samples containing each amine/biocide com-

MWF samples containing each amine/biocide combination were diluted to 5 percent by weight using Lake Michigan tap water.

The differences in fungal control as a function of amine are much greater, with several of the $C_{8\text{-}11}$ compounds performing significantly better than the others.

bination were diluted to 5 percent by weight using Lake Michigan tap water (125 ppm total hardness, chlorinated/fluorinated). A mixed bacterial/fungal inoculum was isolated from field samples of used MWFs. This inoculum was added to 400 mL of diluted MWF in a 500-mL Erlenmeyer flask at a dosage of 1×10^6 colony forming units (CFU/mL) bacteria, and 1×10^4 CFU/mL fungi. A small amount of standard grey cast iron chips was added to the flask, which was then loosely sealed with a polyether foam plug.[7] The flask was mixed continuously on an orbital shaker for five days and then allowed to set undisturbed over the weekend.

This cycling was continued until bacterial and fungal growth exceeded the failure point, indicated by two consecutive weeks at 1×10^5 CFU/mL bacteria or 1×10^3 CFU/mL fungi. Tap water was added as needed to maintain the original fluid volume. The microbial counts were measured weekly using a standard serial dilution/plate count method as described in ASTM Method D5465.

CAST IRON-CHIP CORROSION TEST PROTOCOL

Corrosion of grey cast iron chips in contact with the freshly diluted and microbially-aged MWFs was evaluated using a modified ASTM D4627 procedure. Exactly 3.0 grams of chips were weighed into a small plastic petri dish containing a white filter paper. The chips were covered completely with 5.0 grams of test fluid. The dish was covered with a plastic lid and held at room temperature for two hours. The fluid was removed using a pipet, and the chips dried for 24 hours (on the filter paper in the open petri dish) at 25 C and 60 percent relative humidity. The chips were removed from the filter paper and the percent stain estimated visually.

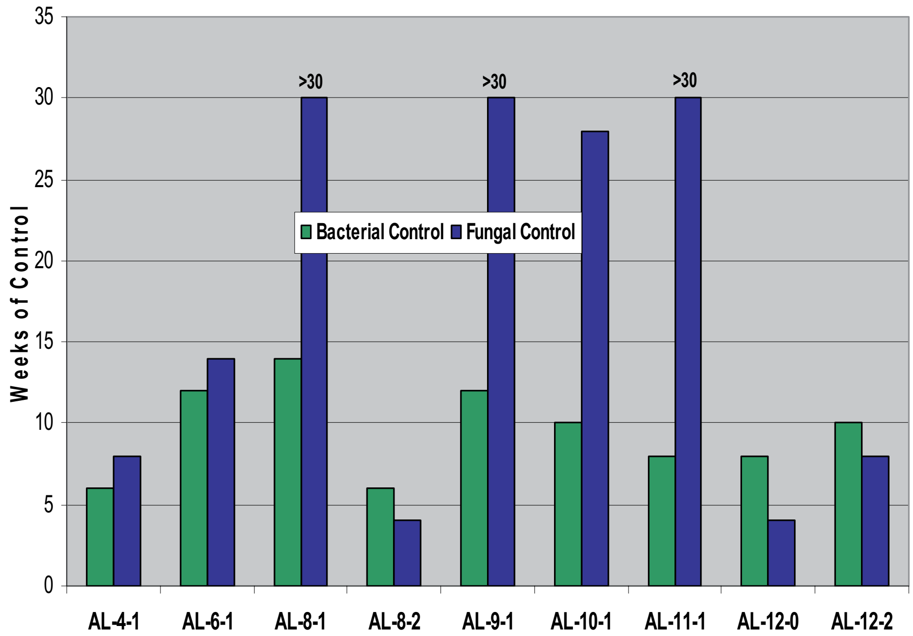

Figure 3 | **Microbial Control with Triazine and Aliphatic Amines**

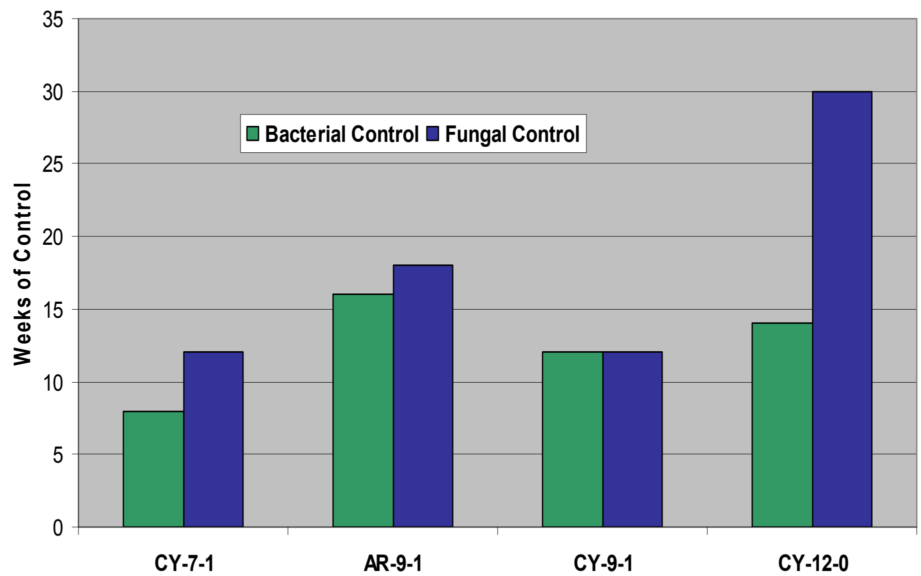

Figure 4 | **Microbial Control with Triazine and Cycloaliphatic/Aromatic Amines**

MICROBIOLOGY AND CORROSION RESULTS WITH TRIAZINE

Results of microbiological testing of fluids with triazine biocide (550 ppm active at dilution) are presented in Figures 3 and 4. These charts present the weeks of bacterial and fungal control as a function of the amine in the formulation (3,000 ppm active at dilution). Figure 3 presents the results with the aliphatic amines. Bacterial control with triazine is better with certain C_{6-12} amines present. One exception is AL-8-2 where the presence of two hydroxyl groups reduces performance relative to a similar compound with one hydroxyl, AL-8-1.

The differences in fungal control as a function of amine are much greater, with several of the C_{8-11} compounds performing significantly better than the others. The performance of AL-8-2 is again inferior to AL-8-1, indicating that the number of hydroxyl groups, in addition to carbon number, is important.

BIT is normally ineffective in controlling bacterial or fungal growth in MWFs.

For the cycloaliphatic and aromatic amines (*see Figure 4*), bacterial control with triazine is in the same range as with the aliphatics, with C_{9-12} performing better than C_7. However, efficacy against fungi is significantly less with the C_9 cycloaliphatic and aromatic amines, and significantly greater with the C_{12} cycloaliphatic amine (relative to aliphatics with the same number of carbons/hydroxyls). The aromatic C_9 amine performs better than the cycloaliphatic C_9.

Cast iron corrosion control data are presented in Figures 5 and 6 for the fresh and microbially-aged fluids. Data for the aliphatic amines (*see Figure 5*) show the best performance with several C_{8-12} amines where initial corrosion control is superior and control is maintained during microbial aging. Exceptions are noted for amines with two hydroxyls (AL-8-2 & AL-12-2) where performance is inferior relative to amines with the same carbon num-

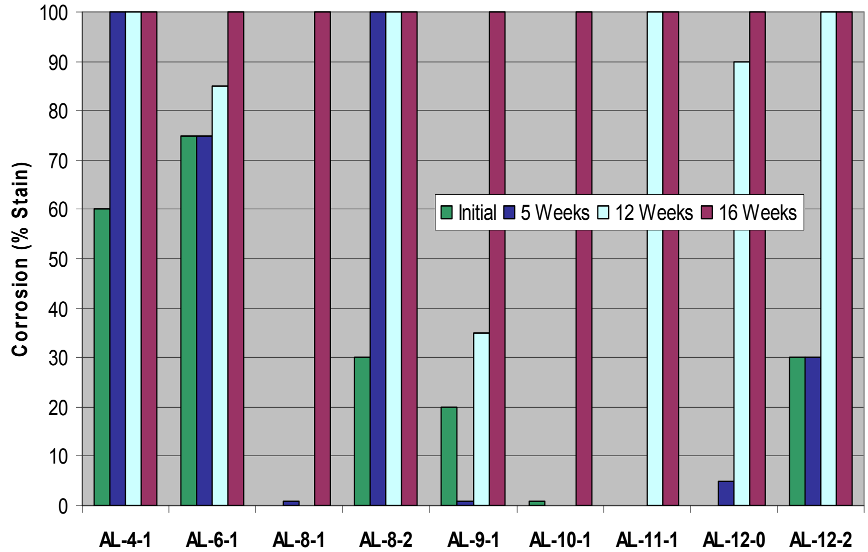

Figure 5 | **Cast Iron Corrosion Control of Fluids with Triazine and Aliphatic Amines**

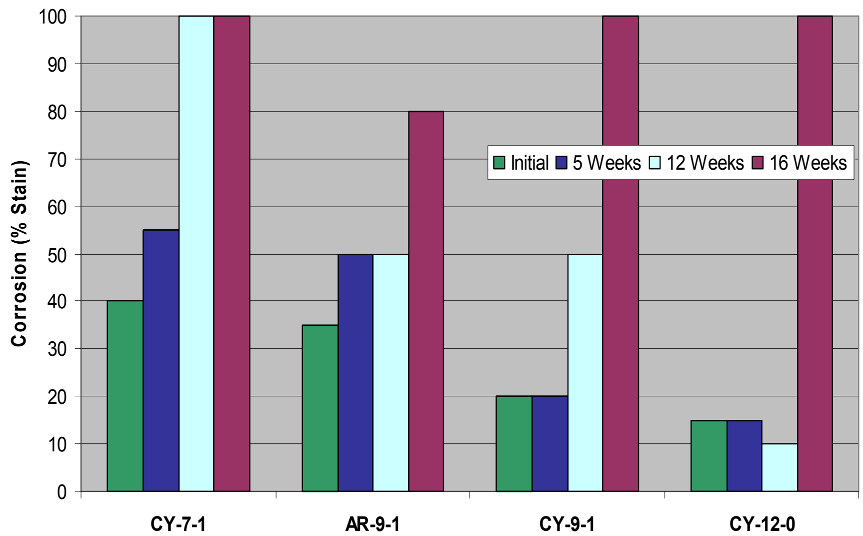

Figure 6 | **Cast Iron Corrosion Control of Fluids with Triazine and Cycloaliphatic/ Aromatic Amines**

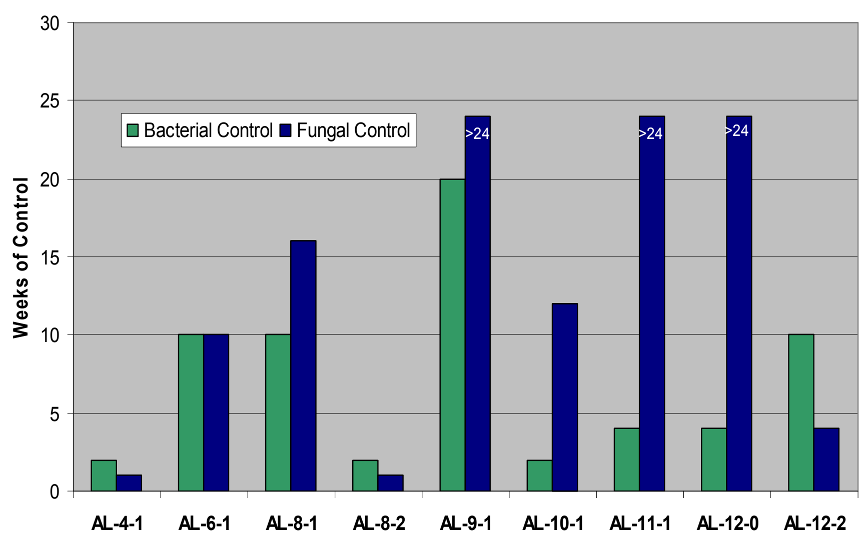

Figure 7 | **Microbial Control with BIT and Aliphatic Amines**

Data for the aliphatic amines show the best performance with several $C_{8\text{-}12}$ amines where initial corrosion control is superior and control is maintained during microbial aging.

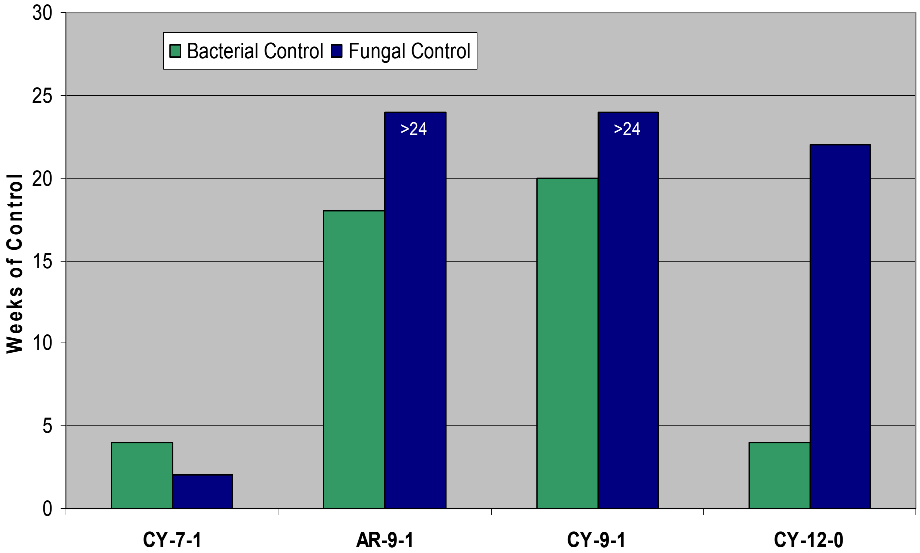

Figure 8 | **Microbial Control with BIT and Cycloaliphatic/Aromatic Amines**

knowledged in the industry as one of the more bioresistant products available. Significant improvements in BIT performance are seen when several of the $C_{8\text{-}12}$ aliphatic amines are used. AL-9-1 performs particularly well with BIT. Performance deficiencies are again noted with amines having two hydroxyl groups (AL-8-2 and AL-12-2) versus those with 0-1 hydroxyls.

For the cycloaliphatic and aromatic amines (*see Figure 8*), the C_9 molecules are best with BIT and perform similarly to the best aliphatic, also a C_9 (AL-9-1).

Cast iron corrosion control data are presented in Figures 9 and 10. Performance is best for fluids with certain $C_{8\text{-}12}$ aliphatic amines, and generally decreases when two hydroxyl groups are present (versus 0-1). The results indicate amines in this range provide inherently better corrosion control, and maintenance of corrosion control correlates well with microbial control.

For the cycloaliphatic and aromatic amines, performance is best at

ber but fewer hydroxyls. This appears to be due to a combination of poorer inherent corrosion control properties and poorer microbiological control.

With the cycloaliphatic amines (*see Figure 6*), cast iron corrosion control is similar to aliphatics with the same number of carbons/hydroxyls. The aromatic C_9 amine is less effective than its aliphatic/cycloaliphatic analogues, however, this amine provides the best corrosion control at the longest microbial aging time. This could be related to the superior bacterial control in this fluid at the 15-16 week period.

When all microbiological and corrosion data are considered, the aliphatic amine AL-8-1 performs best overall with triazine biocide.

MICROBIOLOGY AND CORROSION RESULTS WITH BIT

BIT is normally ineffective in controlling bacterial or fungal growth in MWFs. However, because this biocide is not formaldehyde-based and is stable at alkaline pHs, MWF producers would like to use it where formaldehyde-based products are undesirable or not allowed due to regulation.

Microbiological control results for fluids containing 180 ppm BIT and 3,000 ppm amine (active basis at 5 percent dilution) are presented in Figures 7 and 8. The ineffectiveness of BIT is demonstrated in the fluid with amine AL-4-1 (*see Figure 7*); this amine is ac-

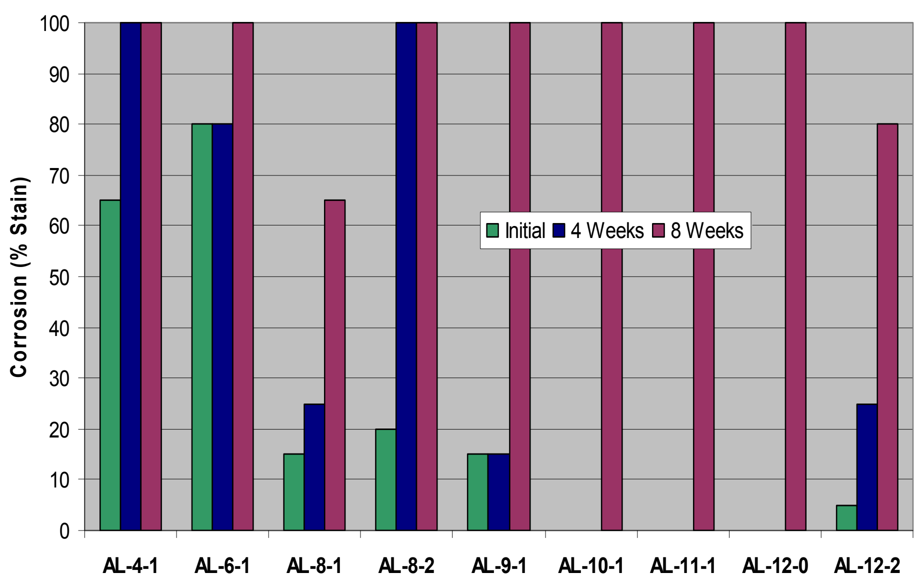

Figure 9 | **Cast Iron Corrosion Control of Fluids with BIT and Aliphatic Amines**

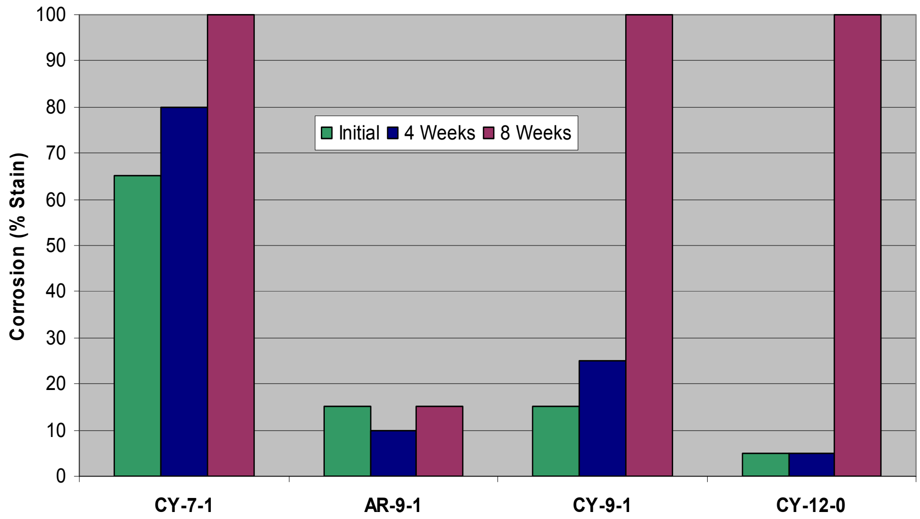

Figure 10 | **Cast Iron Corrosion Control of Fluids with BIT and Cycloaliphatic/Aromatic Amines**

$C_{9\text{-}12}$. The advantage of the C_9 aromatic (versus C_9 cycloaliphatic) was not expected based on the microbial control results. This could indicate less biodegradation of the aromatic, but other explanations are also possible.

When all microbiological and corrosion data are considered, the aromatic amine AR-9-1 performs best with BIT.

CONCLUSIONS

Amine molecular size, structural configuration and number of hydroxyl groups have been shown to influence the performance of two common biocides: triazine and BIT. These factors also influence the inherent corrosion control provided by these amines, as well as maintenance of corrosion control.

Amines in the $C_{8\text{-}12}$ range with 0-1 hydroxyl groups enhance biocide performance more than those outside this carbon range and/or with 2-hydroxyl groups. $C_{8\text{-}12}$ amines also provide the best cast iron corrosion control. The best overall performance with triazine is with a C_8 aliphatic amine, and with benzisothiazolinone a C_9 aromatic amine performs best.

ACKNOWLEDGMENTS

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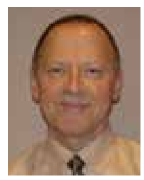

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REFERENCES

1. Byers, J.P. (2006), *Metalworking Fluids, Second Edition*, CRC Press, pp. 132, 138-141, 144.

2. Bennett, E.O. (1979), "Antimicrobial Properties of Butanolamines and Propanolamines in Metalworking Fluids," *J. Gen. Appl. Microbiol.*, **25**, pp. 63-69.

3. Bennett, E.O. (1979), "Corrosion Inhibitors as Preservatives for Metalworking Fluids Ethanolamines," *Lubrication Engineering*, **35** (3), pp. 137-144.

4. Oppong, D. (1989), "Use of a Mixture of Alcoholamines to Potentiate the Antimicrobial Activities of Certain Cutting Fluid Preservatives," *Tribology International*, **22-5**, pp. 343-346.

5. Sandin, M. (1992), "The Role of Alkyl Chain Length on the Antibacterial Activity of Alkyl Ethanolamines," *Biomedical Letters*, **47**, pp. 85-92.

6. Rossmoore, H.W. (1993), "Biostatic Fluids, Friendly Bacteria and Other Myths in Metalworking Microbiology," *Lubrication Engineering*, **49** (4), pp. 253-268.

7. Plugs supplied by Jaece Industries, Inc., North Tonawanda, N.Y., Part number L800-C.

Dr. Frederick J. Passman

Current trends in MWF microbicides

Despite half a century of industrial usage, many unanswered questions remain about the future of these critically important chemicals.

KEY CONCEPTS

- Petroleum companies began researching pathogenic microorganisms in water-miscible MWFs in the 1940s and '50s.
- The Clean Water Act was one of two watershed events that transformed the MWF microbicide market in the early 1980s.
- Although the number of available MWF microbicide products will remain stable or increase slightly over the next several years, the total number of active ingredients will shrink.

METALWORKING FLUID MICROBICIDES (ALSO KNOWN AS BIOCIDES OR, IN REGULATORY PARLANCE, ANTIMICROBIAL PESTICIDES) are chemical substances used to protect MWFs from biodeterioration. As explained in ASTM E-2169[1], microbicides can be used to control microbial contamination in fluid-blending systems (tanks, etc.), as preservatives during in-drum storage or as performance chemicals in application. Although the use of organic antimicrobials dates back to the invention of para-chloro-meta-xylenol (PCMX) in 1889, routine use of microbicides began in earnest in the mid-20th Century.

Three trends drove this mid-century growth. First, the use of water-miscible fluids (any MWF in which the concentrated product is diluted in water, either by emulsification, dissolution or a combination of both) increased dramatically during the pre-World War II period, as both the automotive and aviation industries began to blossom. Growth in numbers of manufacturing plants was coupled with the trend toward the construction of large central cooling systems. Greater volumes, production rates and sophistication of fluid formulations provided an impetus to protect those formulations against biodeterioration.

In the 1940s and 1950s, several petroleum companies sponsored studies on the presence of potentially pathogenic microorganisms in water-miscible MWFs. Not surprisingly, opportunistic pathogens were recovered from the most-used MWFs (E.O. Bennett frequently observed that the taxonomic profile of the microbial community in a given MWF reflected the profile of the community in the make-up water used to dilute the MWF concentrate). Despite these trends, microbicides were used sparingly, even begrudgingly, until the late 1970s to early 1980s. They were generally perceived to be non-value added chemicals, used only when foul odors and slime accumulation couldn't be controlled by other means.

Routine use of microbicides began in earnest in the mid-20th Century.

Two watershed events transformed the MWF microbicide market. In the early 1980s, provisions of the 1977 Clean Water Act[2] began to impact the cost of MWF facility waste management. As plant discharges came under national, state and local regulations derived from the National Pollutant Discharge Elimination System, the cost per gallon of waste treatment approximated and in some localities exceeded that of the original MWF concentrate. This created a strong impetus for increasing fluid performance life.

During the same period, a number of MWF compounders introduced the concept of fluid management. In the pre-fluid management era, typical MWF system draining intervals ranged from two to four months. Companies promoting fluid management programs promised to extend fluid life substantially. Depending on fluid turnover rates, contaminant removal systems, condition monitoring and tankside additions, some systems could operate for years between full draining and system clean out. The effective use of MWF microbicides played a significant role in fluid life extension. Additionally, the period 1965 to 1985 marked the introduction of most of the approximately 80 active ingredients currently approved by the U.S. EPA for use in MWF[1].

In the United States, microbicide use has been regulated since 1910. Initially, use was regulated under the 1910 Federal Insecticide Act. The 1947 Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) made the process of registering and use reporting more stringent. Since 1947, FIFRA has been revised on a number of occasions. Until the EPA was created in 1970, the U.S. Department of Agriculture had responsibility for managing the registration and use of all pesticides. The EPA's Office of Pesticide Programs has administered pesticide regulations ever since. Periodic data recalls have had a substantial effect on both the variety of active ingredients and number of microbicide manufacturers in the MWF industry. For example, after the 1986 data recall, approximately half of the active ingredients with MWF end-use sites (a "site" is a permitted use) disappeared from the list, the number of companies with primary registrations for hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine (HTHT; CAS No. 4719-04-04) shrank from 16 to four. These are registrations as manufacturers, as opposed to supplemental registrations, which include authorization for companies to repackage and sell the product under their private label.

When faced with a data recall, manufacturers can choose to discontinue production of the product, develop the data as required by EPA or negotiate with EPA to define precisely what EPA needs in order to appropriately satisfy the agency's risk-assessment requirements. Historically, data recalls have tended to reduce the number of active ingredients approved for use as MWF microbicides and the number of companies manufacturing products for sale into the MWF market. This trend has reflected each manufacturer's return on investment assessment.

European Union implementation of the Biocidal Products Directive (BPD[3]) and REACH[4] have further complicated the regulatory atmosphere for MWF microbicides. The BPD precedes REACH by nearly a decade. It is similar to the U.S. EPA's FIFRA-based regulations. As with the FIFRA registration process, a battery of environmental fate and persistence, and toxicological tests must be submitted as part of the registration application package. The types of toxicological tests depend on a product's toxicity and the anticipated exposure risks.

One of the major implications of REACH is that it might require essentially the same environmental persistence and toxicological data as currently required under the BDP for all chemicals sold into or manufactured within the EU. The cost of developing a full environmental fate and persistence; toxicology data set can exceed $2 million U.S. The details regarding the types of toxicological tests to be required under REACH remain in flux; however, from the perspective of the microbicides market, it would level the playing field between registered microbicides and unregistered products whose primary function is MWF preservation.

In the prefluid management era, typical MWF system draining intervals ranged from two to four months.

TODAY'S MWF MICROBICIDES

As noted above, approximately 80 active ingredients are currently approved by EPA for use in MWF[1]. However in practice fewer than a dozen active ingredients account for more than 90 percent of the total volume of MWF microbicide use.

First introduced in 1924, HTHT remains the most widely used MWF microbicide in the U.S. Seven manufacturers—four of whom are active in the MWF market—hold primary FIFRA registrations. HTHT remains a high-volume product because of its low cost and versatility. It is a water-stable bactericide that can be formulated stably into emulsifiable-oil, semisynthetic and synthetic MWF and can be used as a tankside treatment.

Although it is still used widely, HTHT has several vulnerabilities. It is a member of the formaldehyde-condensate, formaldehyde-release microbicides. It is manufactured by reacting of formaldehyde and methyl ethanolamine. It kills microbes by hydrolyzing to release the formaldehyde, which then reacts with cell proteins. Since the mid-1980s it has been well-known that many common MWF microbes can become resistant to formaldehyde. This translates into reduced HTHT efficacy.

In the early to mid-1990s, and again over the past couple of years, concerns over formaldehyde toxicity have raised the threat of a total ban on the use of formaldehyde-release microbicides in MWF. My comparison of the toxicological profiles of various MWF microbicides[5] and Howard Cohen's investigation of formaldehyde in the MWF environment[6] seemed to have cooled the 1990s hysteria. However, a decade later, the issue has returned.

In response to concerns about the potential cancer risk associated with incidental exposure to formaldehyde released from formaldehyde-condensate microbicides used in MWF, the EPA's Office of Pesticide Programs is considering imposing a requirement for full carcinogenicity studies for formaldehyde-condensate microbicides. Carcinogenicity studies are lifetime (typically two-year) experiments run on laboratory animals. Post-mortem, the test animals are autopsied to determine the range of effects of exposure to the test substance. These studies can cost more than $2 million.

A pending U.S. EPA registration review for HTHT is likely to require HTHT manufacturers to submit new data for the complete battery of acute, sub-chronic and chronic toxicity tests (estimated cost $4 million). Moreover, EPA is considering lowering the maximum permissible HTHT dosage to 500 ppm; well below the effective dose. These two measures could effectively remove HTHT and other formaldehyde-condensate microbicides from the U.S. MWF market. Several trade organizations are working hard to convince EPA that the existing toxicological data do not support such draconian measures.

Oxizolidines, hydantoins and other formaldehyde-condensate microbicides in addition to HTHT would be affected by this EPA action. It's likely that the variety of antimicrobial products would shrink if carcinogenicity studies were required.

Speculation that the acid fact bacterium *Mycobacterium immunogenum* is the primary agent responsible for the respiratory disease, hypersensitivity pneumonitis (HP), led several major automotive manufacturers to ban or severely limit the use of HTHT in MWF formulations. For reasons explained in my 2008 paper,[7] an untested hypothesis that *M. immunogenum* only grew when the so-called *normal* population (microbes that formed visible colonies on nutrient media within two-to-three days) was suppressed gained wide acceptance for a period. Since HTHT did a good job of controlling the normal population, there were industry stakeholders who concluded that general microbial control was somehow a bad thing.

It is now generally recognized that *M. immunogenum* is one of approximately a dozen microbes that are commonly recovered from MWF and known to cause HP. Also, it has been demonstrated that the prevalence of *M. immunogenum* is unrelated to the prevalence of other microbes in MWF. Moreover, it has been shown that aldehyde-based microbi-

Periodic data recalls have had a substantial effect on both the variety of active ingredients and number of microbicide manufacturers in the MWF industry.

cides (formaldehyde-release and glutaraldehyde) denature endotoxin, but other antimicrobial chemistries do not. However, the ban on in-formulation use of HTHT persists at some metalworking facilities. This is not an endorsement of HTHT. It's simply a polemic against letting hysteria guide technical decisions. When considering the risk associated with the use of certain substances, it's equally important to consider the risks associated with *not using* those substances.

The second major class of MWF microbicide chemicals in current use is the isothiazolines. The first isothaizolin-3-one to gain acceptance as a MWF microbicide was Rohm & Haas' (now part of the Dow Chemical Co.) blend of 5-chloro-2-methyl-4-isothazolin-3-one (CIT; CAS 26172-55-4) plus 2-methyl-3(2H)-isothiazolin-3-one (MIT; CAS: 2682-20-4). The CIT/MIT combination is an effective bactericide at less than 20 ppm active ingredient. However, it hydrolyzes quickly in the presence of primary amines. Consequently, historically CIT/MIT has been used only as a tankside treatment. There are now stabilized formulations of CIT/MIT that can be used in-formulation. Initially, there were a number of patents protecting both the CIT/MIT chemistry and its applications. As these patents have expired, new manufacturers have entered the market. Although CIT/MIT is the best known isothiazoline, a family of isothiazolines has been developed over the past 20 years.

Figure 1 | **Three samples from a series of 15; 20 weeks after having been diluted to end-strength (5 percent v/v). Sample 1 was prepared using tap water, but contained no microbicide. Sample 10 was treated with a microbicide and was filtered periodically. Sample 9 was similar to sample 10 except that it was diluted with high-quality (reverse osmosis) water and its pH was maintained at 9.2. Among the 15 samples only those that contained microbicide retained appearances similar to those of samples 9 and 10. The other 12 samples appeared similar to sample 1 at the end of 20 weeks.** *(Courtesy of STLE member John Burke)*

Although products based on 1,2-benzisothizoline-3-one (CAS 2634-33-5) arrived on the scene nearly a decade before the CIT/MIT blend, their use in MWF was negligible until the mid-1990s. Unlike CIT/MIT, BIT is stable in MWF formulations, but 500 to 700 ppm active ingredient is needed in order to achieve effective antimicrobial activity. Moreover, in contrast to either HTHT or CIT/MIT, BIT performance is MWF formulation dependent. Several isothiazolines are used primarily as fungicides (for example: 2-n-octyl-4-isothiazonline-3-one (CAS 26530-20-1) and n-butyl-1,2-benzisothazolin-3-one (CAS 4299-07-4)).

The isothiazoline fungicides are niche products compared to the two primary chemistries used to control fungal contamination in MWF. For years, sodium-2-pyridinethiol-1-oxide (NPT; CAS 3811-73-2) was essentially the only MWF fungicide in general use (there were a few niche products, but none represented a significant market share).

In the late 1980s, a 20 percent active dispersion of 2-iodo-2-propynylbutyl carbamate (IPBC; CAS 55406-50-6) was approved for use in MWF. The two actives still dominate the emulsifiable-oil and semisynthetic sectors, but NPT remains the dominant product used to protect synthetic MWF from fungal contamination.

In addition to PCMX, two other phenolic products have been used in MWF: sodium para-chloro-meta-cresolate (PCMC; CAS 15733-22-9) and ortho-phenylphenol (OPP; CAS 90-43-7). The popularity of the phenolics has waxed and waned over the years. When chlorinated phenols in water discharges became regulated, all phenolics fell out of favor. Only a few MWF compounders continued to formulate with phenols through the 1980s and 1990s.

However, in the late-1990s, phenolics were regentrified. Their lipophylic properties made them excellent candidates for penetrating the high-lipid content cell-membranes of mycobacteria. Moreover, PCMC has recently received an H-1 certification (approval for incidental food contact) by NSF, so that it can be used legally to protect food-grade lubricants against microbial contamination.

STATE OF PLAY

Over the past 10 to 15 years there has been considerable consolidation among microbicide manufacturers. Arch Chemicals, BASF, Dow Chemical and Troy Chemical have each expanded their biocidal product lines through acquisitions. Given the cost of bringing a microbicide to market, it's likely that further consolidation will occur. The two other major

MWF microbicide suppliers are Buckman Laboratories and LANXESS.

The expansion of product lines reflects a trend toward customer focus. Historically, U.S. microbicide manufacturers only marketed products for which they were the primary producers. Today there is greater emphasis on offering a variety of actives and on developing blends of active ingredients or improved active ingredient delivery systems (for example, using low-volatile organic compound solvents and improving the solubility/dispensability of the active ingredient in different types of MWF).

There's a running debate on where microbicides should be added to MWFs.

The BPD is likely to affect the U.S. MWF market bidirectionally. European companies that have invested to develop BPD toxicological data packages are likely to use these data to support U.S. EPA registrations. This could result in the availability of new active ingredients in the U.S. The major U.S. manufacturers are supporting BPD registration of their products. Because BPD registration satisfies the requirements of REACH, MWF compounders will be able to sell products that have been formulated using microbicides purchased from U.S. manufacturers.

Although the major MWF microbicide manufacturers do a good job of supporting their customers, the MWF market is an orphan biocide market. Microbicide sales into this sector are dwarfed by sales into other markets such as household and institutional products, water treatment and coatings. With the cost of introducing a new active ingredient approaching $4 million just for the data needed to support a registration application, it is unlikely that a new active ingredient will be developed principally for use in MWF. New chemistries will be introduced only after they have been proven successful in larger markets. This trend is exacerbated by the virtual disappearance of non-agricultural microbicide research and development. At most companies, R&D departments have shrunk to the point that the remaining technical staff members have little time to do more than technical support. This scenario is not conducive to new product development.

Beyond the regulatory costs and shrinking R&D efforts of microbicide manufacturers, a historical market dynamic continues to have an adverse impact on MWF microbicide innovation. It's the use of chemicals that are not registered as biocides but whose function is primarily microbicidal. Under FIFRA, pesticide registration is required only for products whose intended use is as a biocide. The logic behind this is not unsound. For example, strong inorganic acids (consider concentrated sulfuric acid) can be extremely toxic. Since they are not normally used to control pests, they do not need to be registered as biocides.

For certain chemicals, the distinction is less clear. Consider dicyclohexylamine (DCHA; CAS 101-83-7). Like other primary amines, DCHA has a high pH (11) and pK_a (10.4). Compounders using DCHA can claim that it is being used solely as a neutralizing amine. However, in reality, DCHA is used primarily to confer biostability on MWF formulations. Phrased less delicately, it's being used as an unregistered antimicrobial pesticide. Since the cost of toxicological and environmental fate and persistence testing for chemicals other than those registered as pesticides is a fraction of that required for pesticides, unregistered products are typically less expensive.

Several compounders have discussed the risks associated with DCHA use in MWF.[7] Other products, some of which had FIFRA registrations prior to the 1986 data recall but whose manufacturers decided not to support retaining their registrations, continue to be marketed as buffering agents. Less toxicological data, however, does not translate into less risk. It simply reduces the incentive of microbicide manufacturers to bring new active ingredients into the marketplace.

THE FUTURE

More likely than not, although the number of available MWF microbicide products will remain stable or increase slightly over the next several years, the total number of active ingredients will shrink. In particular, with the possible exception of HTHT, formaldehyde-release products approved for tankside application are likely to disappear if manufacturers are required to develop life-cycle toxicity/carcinogenicity data. Unless the trend in research department spending is reversed, the level of technical support provided by microbicide manufacturers will diminish over time.

There's a running debate on where microbicides should be added to MWFs. Some end-users are adamant that microbicides should only be used tankside so that microbes in MWF

The details regarding the types of toxicological tests to be required under REACH remain in flux.

systems won't become resistant to the treatment chemicals. Others are equally adamant about not using any microbicides tankside. They object to the inconvenience of tankside additions and to the potential health risks associated with having their workers handle biocide concentrates in the plant. From a performance perspective, those who insist on tankside additions are on firmer footing.

The concentration of active ingredient that is present in diluted MWF depends on the concentration at which it was added to the MWF concentrate, its stability in the concentrate, the end-use concentration of the MWF product and the various demands on the microbicide in the MWF system. The concentration of microbicide added to a MWF formulation is limited to the range that has been approved as part of the product's FIFRA registration. Microbicide stability in concentrate is affected by the MWF's total chemical composition, storage conditions and time between production and use. The microbicide concentration that's appropriate for a MWF used at 7 percent is likely to be insufficient when the same MWF is used at 3 percent. Conversely, it may exceed the permissible dose level for a MWF used at 3 percent if the microbicide was formulated for a MWF used at 7 percent.

Finally, it is impossible to predict all of the demands (all factors that consume biocide molecules) on a microbicide in end-use application. Water-quality, metalworking operations and industrial hygiene practices all affect the rate at which microbicides in MWF are consumed. When handled in accordance with manufacturers' recommendations, microbicides can be used safely as tankside additives.

Industry stakeholders are becoming more aware of the need to control both biofilm development and bioaerosol generation. Historically, the focus has been on controlling the numbers of microbes in recirculating MWF. Unless the biofilm community is also controlled, microbe numbers drop briefly then increase rapidly after biocide treatment. Moreover, the mechanism of biocidal action is likely to affect both the total amount and composition of bioaerosol in MWF mist. Over the next few years, I anticipate that industry stakeholders will consider the effects of biocides on biofilm and bioaerosols as part of the product selection process.

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REFERENCES

1. ASTM Standard, E-2169 (2007), "Practice for Selecting Antimicrobial Pesticides for use in Water-Miscible Metalworking Fluids," ASTM International, West Conshohocken, Pa., 2003, DOI: 10.1520/E2169-01R07, **www.astm.org**.

2. Code of Federal Regulations, 40 CFR 122, EPA Administered Programs: The National Pollutant Discharge Elimination System.

3. Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 Concerning the Placing of Biocidal Products on the Market

4. (EC) No. **1907/2006** of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACh).

5. Passman, F.J. (1996), "Formaldehyde Risk in Perspective: A Toxicological Comparison of Twelve Biocides," *Lubrication Engineering*, **52** (1), pp. 68-80.

6. Cohen, H.J. (1995), "A Study of Formaldehyde Exposures from Metalworking Fluid Operations using Hexahydro-1,3,5-Tris (2-hydroxyethyl)-S-Triazine," In. J.B. D'Arcy, Ed., *Proceedings of the Industrial Metalworking Environment: Assessment and Control*. American Automobile Manufacturer's Association, Dearborn, Mich., pp. 178-183.

7. Anonymous (2006), "Controlling Microbial Growth… Safely," Milacron Marketing Co., Cincinnati, Ohio.

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SOUNDING BOARD

What is the biggest issue facing the metalworking fluids industry today?

The Globally Harmonized System (GHS) of Classification and Labeling of Chemicals, already in place in some parts of the world and slated for 2015 adoption in the U.S., is on the minds of TLT readers, according to responses to this Sounding Board survey. The education process already is under way, with 27 percent of readers saying they are confident in their GHS knowledge. Other readers are concerned about the dwindling number of chemicals that can be used in metalworking fluid formulation, with several respondents citing the loss of boron in particular. "It's like trying to make the same words with fewer and fewer letters in the alphabet!" says one. The pressure of complying with ongoing and ever-changing regulations remains a challenge. Says one reader: "There is no one controlling body. Rather, it's a cornucopia of states and countries, each with a different focus or concern." Also mentioned by several readers is the lack of worker training about the proper use of MWFs. Poor education can increase the risk of health issues to workers and prevent the fluid from performing at its highest level.

Excellent relation price/technology!

Global Harmonized Standard mislabeling. Lots of potential for confusion and mistakes.

Banning of additives used in the fluids. Very difficult to find alternatives.

Separating specialty product claims from good science.

Environmental and health issues.

Quality and productivity.

Lack of adequate housekeeping in the plants.

The biggest issue facing us in the industry is the progress toward more environmentally friendly types of products and the cost of raw materials.

Replacing chlorinated paraffin with more environmental friendly additives.

Regulation, especially with regard to triazine, boric acid and the insane pictograms required for the safety data sheets. Really? If you can't read the MSDS, you shouldn't be using industrial chemicals, metalworking fluids, etc. Pictures will only confuse people, and what a mess for us to have to incorporate them on everything.

Environmental issues such as waste disposal.

Distribution and technical knowledge support.

Skilled people/staff to make the fluid perform at the highest level possible.

Health issues such as fumes around the work site. Environmental pollution issues.

Constituents and the health and safety legislation affecting them.

Restriction by legislation for biocide; uncertain situation about usage of boric acid.

Handling boron-free chemistries and low/no-formaldehyde release biocide chemistry.

Monitoring of the MWF by the operator of the machines. Our customers fail to see the advantages of monitoring.

CARB in Southern California. We had to remove products instead of trying to comply with the regulations.

REACH ECHA. Substitution of substances.

The adverse impact of MWF on the environment and how to handle these to achieve the "zero discharge" targets attempted by some plants.

The major issue is the lack of fundamental understanding about emulsion formation and properties, especially lubricity and rust protection. Technical personnel do not know why one product works and another does not. As a result, MWF sales mostly rely on marketing and not on the lubricant quality.

There is no consistency in the performance of the products. Customers have now gone into the mode of price instead of cost per component. Also the slowdown in auto sector and volatility in the base oil market is making it tough for manufacturers to sustain their margins.

Extending the life of a MWF.

Cost of regulatory compliance.

Knowledge on how to properly handle MWFs at the customer's facility by the employees who use the fluids (concentration, cleanliness, contamination, bacteria, etc.)

Environmental challenges in that there is no one controlling body. Rather, it's a cornucopia of states and countries, each with a different focus or concern.

EPA and other government agencies. Will we still be able to manufacture in the U.S.?

Worker health and safety.

Long-lasting coolants that do not produce odors and last for a long time while producing excellent tool life and corrosion protection while minimizing carry off on parts.

End-user friendliness, safety.

Permanent cost pressure, higher customer leverage.

Low sales! No business!

Environmental constraints causing an increase in tooling costs.

Product labeling and the safety data sheets outlined by GHS.

The restrictive California VOC regulations will most likely spread nationwide and push more manufacturers and customers toward green-fluid technologies.

The ever-tightening regulations and restrictions on raw materials.

Governmental guidelines regarding chemicals used within our industry.

High prices. Customers, when confronted, look around, which is not a good thing for me.

The limitation of triazine dosage.

GHS, particularly the confusion over safety data sheets, REACH and BPD dossiers. How they relate to products manufactured or formulated in the U.S. has created considerable confusion.

How well versed do you feel you are about GHS?

I'm confident in my knowledge about GHS	27%
I have a basic understanding but need more information.	37%
What standard?	36%

Based on responses sent to 13,000 TLT readers.

No standardizations or approved products for applications.

Chemical costs regarding disposal, handling, human contact (health concerns).

(1.) The demand for cheaper products and (2.) regulatory issues that cause raw materials to be removed from the marketplace. It is like trying to make the same words or at least synonyms with fewer and fewer letters in the alphabet!

REACH compliance and the Chinese equivalent of REACH.

Imports from developing countries, especially China and India. Some products may not be up to North American standards but are inexpensive.

How to keep products performing while meeting the requirements of regulatory agencies.

Fewer raw materials to work with.

Health issues. Some fluids could make harmful fumes and vapor. Others would sustain bacteria growth, which is a health hazard.

Regulatory restrictions and requirements. Increased cost, over-burdened workforces.

Biocide restrictions.

A number of MWF suppliers in the market producing and supplying low-quality products at a lower price compared with those reputable manufacturers who have been in this industry for years and produce and offer high-quality products and great services.

Bacteria growth.

Regulation of hazardous materials, particularly mists. Developing more environmentally friendly alternatives.

What emerging technologies will most affect MWFs in the next decade and beyond?

A technology that supports all types of public water hard or soft.

Biobased coolants.

New tooling and environmental friendly fluids.

Working materials and tool design.

3D printing.

Getting away from the boron amide technology will have a major impact on MWFs.

The use of other basestocks besides Group I baseoils.

Dry machining.

Extending the life of machine tools.

Proper filtration, new techniques on hazardous-substance handling, PPE.

I am a fan of the near-dry lubrication machining technology concept in MWF.

The need to move to safer, biodegradable and synthetic materials.

New molecules with high biostability but no harm to the environment or humans.

Perhaps more in-line monitoring? Chemical regulation.

Nanotechnology for performance enhancement and efficient treatment techniques to mitigate adverse environmental impacts.

Better synthetic lubricants, better biocides and better tool construction through better materials.

New basestocks, the shift in manufacturing to new and alternate alloys, tooling design and regulatory and registry strangulation.

Surfactant package is the key to MWF. The formulators who can develop synergistic mixtures with good lubricity and RP at high dilutions will dictate the MWF trends.

A robust tool design along with a lubricant source device should give a boost to the MWF sector, as well as the industrial sector as a whole.

Technology surrounding longevity of MWFs and the use of different chemistries that incorporate silver into the formulas and potentially other special metals that aid the ability to fight bacteria and fungus within sumps.

Chlorine-replacement chemistry.

Biobased fluids that are more worker friendly.

The development of formulas that do the job without having to use tank-side additives and biocide/fungicide treatments.

MQL, nano-based fluids.

Machining ceramics or using ceramic tools, porosity and absorption characteristics of materials.

Low VOC basestocks to produce low-VOC MWFs.

Printing may be an issue depending on the speed and development of this technology.

Continued development of synthetic basestocks and performance additives.

Waste and reuse.

REACH, reusing biocides, ongoing regulations and MSDS issues.

3D manufacturing.

Actual testing of chemicals instead of just banning them because one 30-year-old study says they might be harmful 1 percent of the time.

Vegetable base fluids, low-VOC fluids and chlorine removal.

Coatings.

Better recycling processes.

Perhaps better cooling methods will be developed that allow for the use of less mist-intensive alternatives. TLT

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Certified Metalworking Fluids Specialist

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- For individuals working in a manufacturing environment such as a fluid specialist or fluid manager, the requirement is three years.
- For individuals working in a laboratory environment such as a technical support chemist or research chemist, the requirement is five years.

KNOWLEDGE

- **Minimum:** two-year degree in science, manufacturing technology or business; coursework, including general chemistry and biology; minimum 20 hours internal or external training in MWF applications and management.
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STLE University is your personalized, centralized location for continuing education in the field of tribology and lubrication engineering. We provide you with the latest educational information in the field while at the same time providing opportunities to enhance your career and create value for your company.

STLE University was designed with our members in mind. STLE provides education that is:

- **Focused:** STLE offers a variety of courses and webinars that are designed for specific audiences working in the field of tribology and lubrication engineering. Our offerings vary by topical area, level of expertise (basic to advanced) and audience segment (formulators, salespeople, distributors, students, etc.).
- **Flexible:** Courses are available in-person and online to fit around any busy schedule, and are designed to meet your varying educational needs. If you need a short course, an introduction/overview or a long, in-depth course, chances are STLE University has something to fit your needs. There are varying types and formats of courses to match up with your available time commitment.
- **Accessible:** STLE offers a variety of educational opportunities, both in-person and online. Our in-person education locations change yearly, ensuring you have a chance to visit one nearby. Our online options allow you to purchase a course at any time and start it immediately. As long as you have a computer and an Internet connection, you have online education. Also, STLE University is not limited to members. However, you receive significant discounts if you become a member.

All of our educational opportunities also apply towards STLE's recertification requirements. Visit **www.stle.org/university** for more information and schedule of upcoming courses and webinars.

Find out more about STLE! Sign up and follow us on:

Choose from a variety of educational formats:

Online Offerings

- **Online certificate courses**
  - Fundamentals of Lubrication
- **Online short courses**
  - Basic Lubrication
  - Lubrication Composition
  - Fluid Management & Recycling
  - Metalworking Fluids
- **Monthly Webinars**

  Topics include bearings, gears, hydraulics, MWFs and much more!

In-Person Offerings

- Annual Meeting courses
- Local Section courses
- Certificate courses
- On-site education courses

Society of Tribologists and Lubrication Engineers
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