Life After the Big Four

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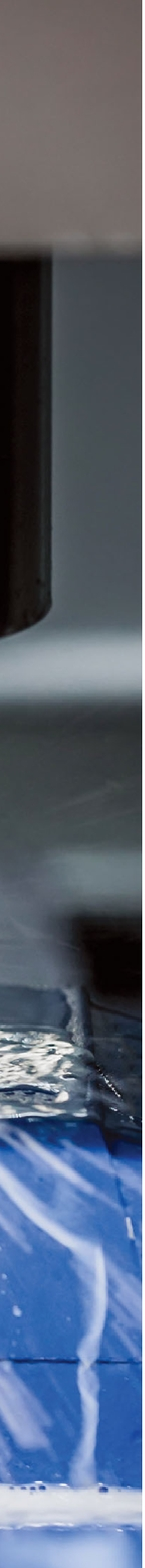
Andrey Armyagov-Fotolia

Will Metalworking Fluids Suffer without Boron, Formaldehyde, DCHA and Phosphorus?

Metalworking fluid suppliers are watching some long-standing chemistries disappear from their toolbox, such as formaldehyde, boron, dicyclohexylamine (DCHA) and phosphorus. This article will show it is possible, even without these “big four” components, to formulate a long-lasting, multi-metal, water-dilutable metalworking fluid.

Formaldehyde condensates, like hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine, have been used for years to provide cost-effective control of bacterial growth in metalworking fluids. Amine-boric acid salts, as well as condensation products, are multi-functional biostatic corrosion inhibitors used in metalworking fluids since the early 1980s. These components have helped metalworking fluid producers provide long-lasting products that resist degradation by microorganisms.

Unfortunately, formaldehyde condensate biocides have the potential to release formaldehyde under metalworking fluid use conditions. The International Agency for Research on Cancer and the National Toxicology Program consider formaldehyde a known human carcinogen.

In 2010, the European Classification, Labelling and Packaging regulation took effect, and under this regulation boric acid is classified as toxic to reproduction, Category 1B. Boric acid has been added to the European Union’s candidate list of Substances of Very High Concern, and its use is limited to less than 5.5 percent by weight in metalworking fluid concentrates. Reaction of certain amino alcohols with boric acid results in the formation of borate esters and other products, which are subject to pH dependent hydrolysis. The amine type, as well as pH, temperature and concentration will influence the rate of hydrolysis and possible re-formation of boric acid.

Metalworking fluid formulators continue to seek chemistries that enable fluid performance to be maintained while complying with regulatory requirements and customer preferences. Non-formaldehyde biocides such as benzisothiazolinone (BIT) are available, but often are less effective than formaldehyde condensates. Products like dicyclohexylamine (DCHA) are used and help extend fluid life significantly in the presence of non-formaldehyde biocides such as BIT. However, under the Globally Harmonized System for hazard communication, DCHA must be labeled with the toxic and environmental hazard pictograms. Some fluid producers and end users prefer to avoid DCHA or require that it not be used.

Finally, fluids formulated for compatibility with iron, steel and aluminum alloys often contain organo-phosphate esters. These esters provide antiwear lubrication, and also prevent staining of aluminum alloys. However, some products can stimulate microbiological growth, and metalworking fluid producers may choose to avoid them if performance objectives can be met in other ways.

Formulating Without

Is it possible to meet demanding performance requirements without the use of formaldehyde condensate biocides, boric acid and boron condensates, DCHA and phosphorus? The authors have shown it is possible using a controlled laboratory study of a low oil semi-synthetic metalworking fluid.

As shown in Table 1, this study created 10 fluids from different ingredients at various concentrations.

- Fluid 1 contains all four components under consideration (triazine, boric acid, DCHA and a phosphate ester).
- Fluids 2 and 3 eliminate these components, using lactic acid in place of

boric, and benzisothiazolinone (BIT) or a morpholine/dimorpholine biocide (MDM) to replace triazine.

- Fluids 4-10 use 3-amino-4-octanol (OA) in place of DCHA, and BIT, MDM or phenoxyethanol instead of triazine; phenoxyethanol is registered under the Biocidal Products Directive in the European Union.
- Fluids 8-10 contain phenoxypropanol as a biostatic coupling agent, in place of propylene glycol n-butyl ether.

Test Methods

All fluid concentrates were diluted with chlorinated city tap water to 5 percent; water hardness was approximately 125 ppm. For each fluid, the authors tracked the following performance characteristics over time:

Microbiological Challenge. The resistance of fluid components to microbiological degradation is a critical factor in metalworking fluid performance longevity. To assess microbial resistance, a modified ASTM E2275 protocol was used. The diluted fluids were placed into Erlenmeyer flasks and challenged weekly with a mixed bacterial/fungal inoculum isolated from spoiled metalworking fluids; the challenge was approximately 1x10^6 colony-forming units of bacteria per milliliter and 1x10^4 CFU/mL fungi. Microbes were added on Monday morning with 3 to 5 percent tramp oil (Ace Hardware Hydraulic Oil), then the fluids were mixed on orbital shakers through Friday afternoon and shut down for the weekend. Separated tramp oil was removed on Monday morning, using filter papers to absorb the oil without removing metalworking fluid.

This process was repeated until failure, defined as two consecutive weeks above 1x10^5 CFU/mL bacteria or 1x10^3 CFU/mL fungi. The pH of each fluid was measured weekly prior to inoculation.

Cast Iron Corrosion. Water dilutable metalworking fluids should prevent corrosion of iron and mild steel, even if these materials are not being machined, because tools may be constructed of these materials. Cast iron is most prone to corrosion, and is evaluated as a worst-case condition.

In our study, cast iron chips were exposed to freshly diluted and microbially aged fluids, using a modified ASTM D4627 procedure. The chips were placed on filter paper, exposed to fluid for two hours (covered), drained and dried for 24 hours at 25 degrees C and 65 percent relative humidity. The test was repeated every four weeks during microbial challenge.

Aluminum Staining. Usage of aluminum alloys for automobile construction is increasing, and metalworking fluids must not discolor or stain them during or after the machining process. The protective oxide on these alloys is prone to degradation at alkaline pH, and certain metalworking fluid components, including amines, can cause staining. In our experience, this is influenced by pH, amine type and total alkalinity. It is possible to make a non-staining fluid at pH 9.5 if the amine type and total alkalinity are properly adjusted.

We measured the staining behavior of fresh and microbially aged fluids by completely immersing aluminum alloys 356, 2024, 6061 and 7075 on watch glasses at room temperature for 24 hours. Fresh fluids often represent worst case, since their pH tends to drop over time due to reaction of amines with dissolved carbon

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Table 1.
Semi-synthetic MWF Formulations

	Fluid									
	1	2	3	4	5	6	7	8	9	10
Ingredient*	Make-Up (%) of Fluid Concentrate									
Hydrotreated Naphthenic Oil	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Sodium Petroleum Sulfonate	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0	14.0
Tall Oil Fatty Acid	6.0	5.0	5.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Aliphatic Dicarboxylic Acid	2.0	2.0	2.0	2.0	2.0					
Cyclic Dicarboxylic Acid		2.0	2.0	2.0	2.0	4.0	4.0	4.0	4.0	4.0
Ether Carboxylic Acid	3.6			6.0	6.0	4.4	4.6	5.2	5.4	6.3
Boric Acid	2.0									
Lactic Acid		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Monoethanolamine (MEA)	4.5	9.2	9.6	7.4	7.8	4.6	5.0	4.6	4.7	4.8
Triethanolamine (TEA)	5.0	6.0	5.0	5.0	5.0					
2-Amino-2-Methyl-1-Propanol (AMP)—95%						3.6	3.6	3.6	3.6	3.6
Dicyclohexylamine (DCHA)	6.0									
3-Amino-4-Octanol (OA)—85%				6.0	6.0	6.0	6.0	6.0	6.0	6.0
Phosphate Ester	2.4									
Synthetic Ester Lubricant		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Propylene Glycol n-Butyl Ether	3.0	3.0	3.0	3.0	3.0	3.0	3.0			
Phenoxypropanol								3.0	3.0	3.0
Triazine—78.5%	2.0									
Benzisothiazolinone (BIT)—20%		2.0		2.0		2.0		2.0		
Morpholine/Dimorpholine Derivative (MDM)			2.0		2.0		2.0		2.0	
Phenoxyethanol										6.0
Deionized Water	39.6	36.8	37.4	26.6	26.2	32.4	31.8	31.6	31.3	26.3
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**
pH @24 Hrs. (5% dilution)	9.45	9.40	9.40	9.41	9.43	9.51	9.44	9.51	9.43	9.50

**All components supplied at ~100 percent active, except as otherwise indicated.*

Source: ANGUS Chemical Co.

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dioxide, and also because of acidic biodegradation products.

Results and Discussion

Results of the microbiological tests are presented in Figures 1 and 2. Fluid 1, formulated with boric acid, formaldehyde-condensate biocide (triazine), DCHA and phosphate ester, resists bacterial attack for 24+ weeks and fungal attack for 21 weeks. Fluid 2, with lactic acid replacing boric, MEA replacing DCHA, BIT replacing triazine, and a synthetic ester replacing phosphate ester, resisted bacteria for nine weeks and fungi for one week. In a similar formulation (Fluid 3) using morpholine/dimorpholine biocide (MDM), bacteria were controlled for 12 weeks and fungi for one week.

Removal of triazine, DCHA and boric acid had a significant negative impact on microbial resistance. The authors believe removal of triazine and DCHA had a bigger impact on microbial resistance than the removal of boric acid, based on previous studies in our laboratory.

The remaining fluids, all containing 3-amino-4-octanol in place of DCHA, resisted bacteria for at least 21 weeks and fungi for at least 19 weeks, regardless of which biocide was used. Fluids 4, 6, 8 and 10 performed best, resisting bacteria and fungi for 24+ weeks. Use of BIT or phenoxyethanol in combination with 3-amino-4-octanol is the common denominator in the best performing fluids.

The lower bacterial and/or fungal resistance of fluids with MDM (Fluids 5, 7 and 9) could be due to greater partitioning of MDM into tramp oil. The octanol-water partition coefficient of BIT at pH 9 is -0.9, meaning BIT prefers the water phase. The partition coefficients for the mono- and dimorpholine derivatives in MDM are 1.12 and 1.98; both prefer the organic phase. Partitioning of MDM from the diluted fluids into tramp oil, and subsequent removal during weekly skimming, is a plausible explanation for the earlier loss of microbial control.

The pH stability results (see Figure 3) correlate with micro-

Figure 1. **Bacterial Control**

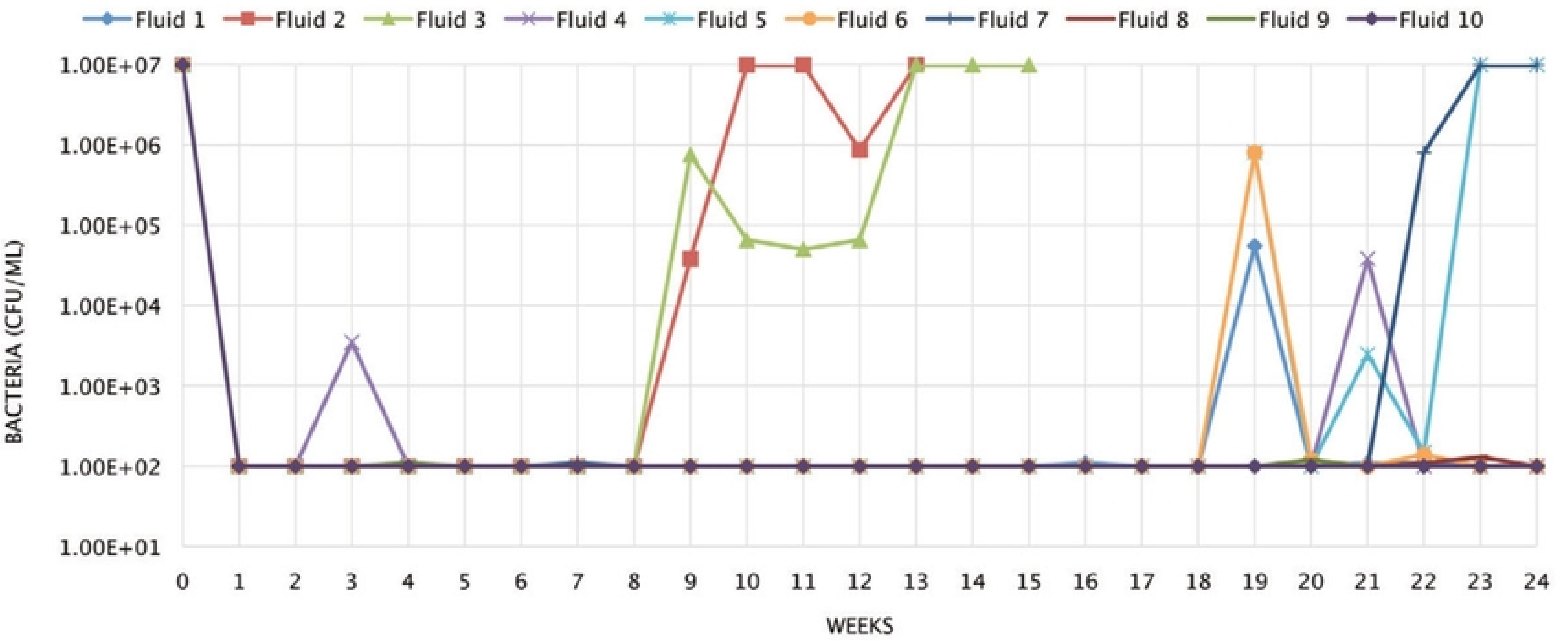

Figure 2. **Fungal Control**

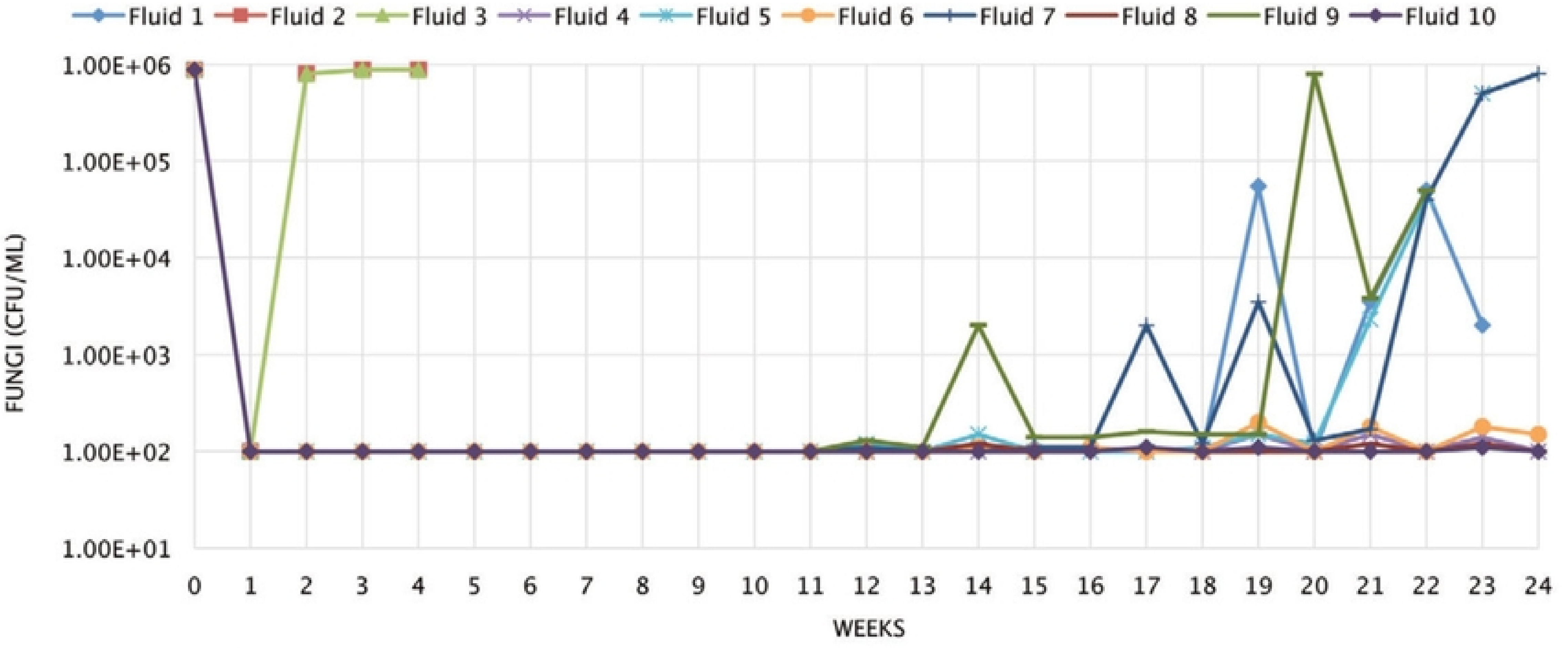

Figure 3. **pH Control**

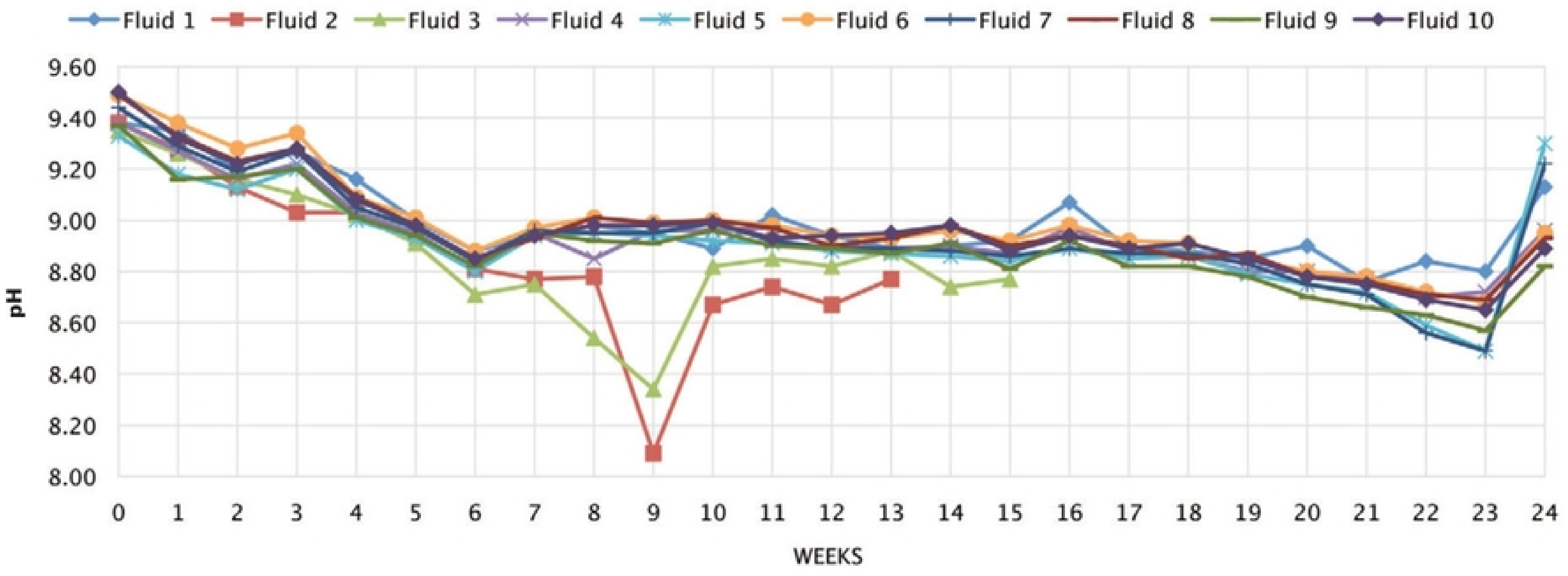

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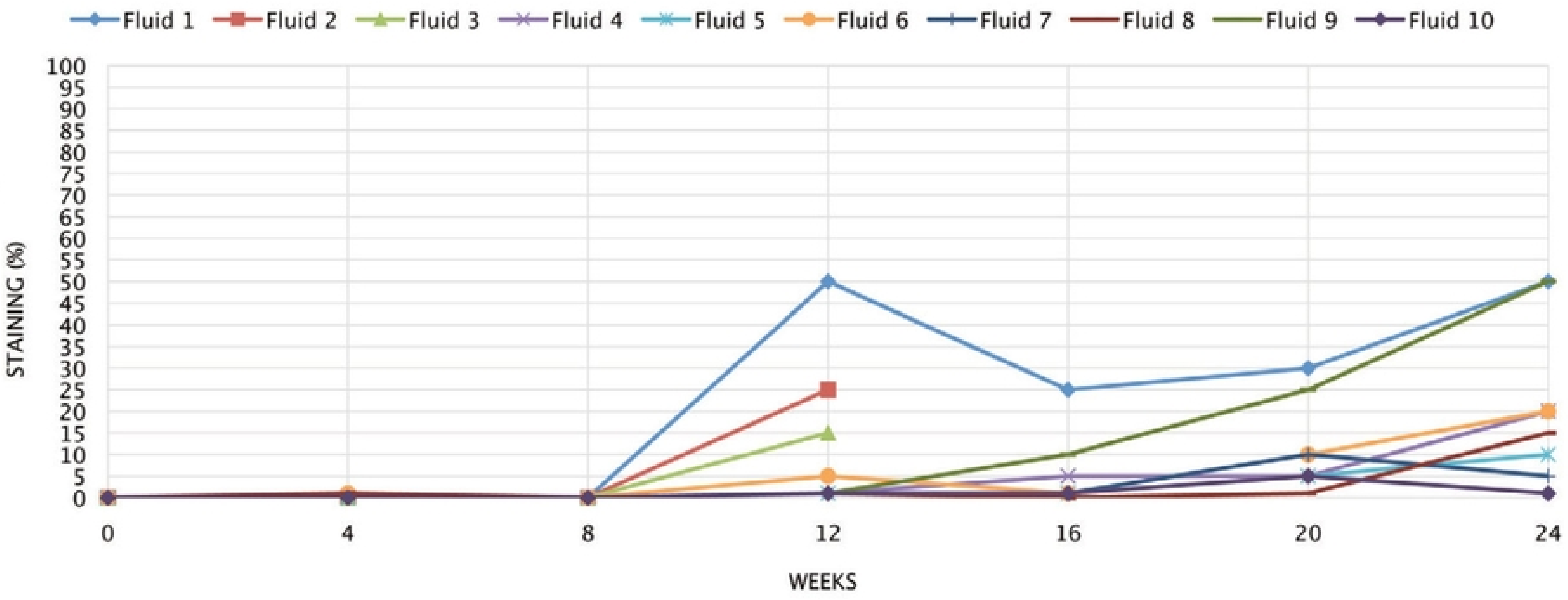
Figure 4. **Cast Iron Corrosion Control**



bial control, as expected; those that failed earlier (Fluids 2 and 3) showed the earliest loss of pH control. The decrease and increase in pH that occurs at 8 to 10 weeks for Fluids 2 and 3, and at 23 to 24 weeks for the others, is believed to be due to formation of alkaline biodegradation products; no deliberate adjustments of pH were made.

Cast iron corrosion results are presented in Figure 4. Initial control was good, however, corrosion with Fluids 1 through 3 began after eight weeks due to microbiological degradation; Fluids 2 and 3 were stopped after 15 weeks due to bacterial and fungal failure. All experimental fluids (4 through 10) provided better control, although staining was observed with Fluid 9 beginning at 16 weeks. In general, microbial and corrosion control correlated well.

None of the fresh or microbially aged fluids stained aluminum alloys 2024, 6061 or 7075. The fresh fluids stained aluminum 356 slightly, but this stopped after four weeks of microbial aging, probably due to the reduction in pH.

Conclusions

The present study has shown it is possible to make a long-lasting, semi-synthetic metalworking fluid without boric acid, DCHA and formaldehyde condensate biocides. Performance can be maintained or even improved, with proper selection of amines and non-formaldehyde biocides. Removal of phosphate ester did not negatively impact aluminum staining, however, the effects on antiwear lubrication were not determined.

The impact of formulation changes on

cost was not calculated, however, at current raw material prices, Fluids 4 through 10 will be more expensive than Fluids 1, 2 and 3. It is possible, even likely, that the increased formulation cost would be offset by longer fluid life and all the associated benefits: reduced downtime, lower fluid replenishment and waste disposal costs, decreased tankside maintenance and labor costs, etc. ■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Bonnie Pyzowski, a senior technologist with over 16 years at ANGUS Chemical Co. in Buffalo Grove, Ill., has a diverse technical background in a variety of industrial/laboratory settings involving research and development expertise in formulating metalworking fluids. She obtained a certificate in chemistry in Poland and is a member of the STLE executive committee in Chicago.

Nicole Webb is a customer application technologist at ANGUS, which she joined last year, supporting new product development for metalworking fluids and performing customer-focused microbiological testing. She holds a bachelor's degree in microbiology/cell & molecular biology from Oklahoma State University, is an ASCP certified medical technologist and a member of STLE.

Pat Brutto is an R&D scientist at ANGUS, leading the development of new technologies for metalworking fluids. He joined the company in 1987, holds an M.Sc. in chemistry from DePaul University, is an STLE certified metalworking fluid specialist and a member of STLE's board of directors. For information, e-mail him at PEBrutto@ANGUS.com or visit www.ANGUS.com.

Further Reading

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