Design of Hard Water Stable Emulsifier Systems for Petroleum- and Bio-based Semi-synthetic Metalworking Fluids

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Metalworking fluids (MWFs) increase productivity and the quality of manufacturing operations by cooling and lubricating during metal forming and cutting processes. Despite their widespread use, they pose significant health and environmental hazards throughout their life cycle. An obvious environmental improvement to MWF technology would be to improve the lifetime of the fluid while utilizing more environmentally friendly and less energy-consuming materials without compromising existing performance levels. This investigation focuses on the design of mixed anionionc:nonionic emulsifier systems for petroleum and bio-based MWFs that improve fluid lifetime by providing emulsion stability under hard water conditions, a common cause of emulsion destabilization leading to MWF disposal. Experimental conditions were designed to evaluate the impact of emulsifier structural characteristics (straight chain, branched tail, branched head) and the molar ratios of anionic to nonionic surfactant and oil to total surfactant. Results from the 2500 formulations generated indicate that the use of a twin-headed anionic surfactant can provide improved hard water stability for both mineral oil- and vegetable oil-based formulations, even in the absence of a chelating agent and a coupler. Results also suggest that an oil:total surfactant molar ratio of 0.5 or less is necessary for particle size stability in hard water conditions for these systems. The newly developed petroleum and bio-based formulations with improved hard water stability are competitive with commercially available MWFs in performance evaluations for tramp oil rejection, contact angle, and tapping torque efficiency. These results can be used to design MWF formulations with fewer components and extended lifetime under hard water conditions, both of which would lead to a reduction in the life cycle environmental impact of MWFs.

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Introduction

Metalworking fluids (MWFs) increase the productivity and the quality of manufacturing operations by cooling and lubricating during metal forming and cutting processes (*1*). Despite their widespread use, MWFs pose significant health and environmental hazards throughout their life cycle. Growing realization of these hazards has resulted in increasingly strict worker safety and environmental regulations and higher costs for metals manufacturers (*2*). One potential way to avoid these environmental impacts is to discontinue or limit the use of MWFs. While this can eliminate the costs and environmental impacts associated with MWF use, replacing MWF function has proven challenging (*3*–*6*), and dry/damp machining may carry with it negative environmental and economic impacts of its own. Given that the machining of metal is essential to modern society and that MWF use is continuing to grow, it is necessary to design MWF systems with minimum impact on the environment.

In this paper, MWFs with the potential for greatly extended in-service lifetime relative to existing MWFs are designed using an approach consistent with the Principles of Green Engineering (*7*). The most significant contributions of this research include the substitution of MWF components with alternatives that are more inherently benign (Principle 1) and the prevention of premature MWF failure leading to excessive environmental disposals (Principle 2). The paper also describes technical research related to other strategies for green design. For instance, the new MWF formulations developed during this research can utilize oil and nonionic surfactants based on renewable resources (Principle 12). These formulations are designed for oil separation, recovery, and reuse through the use of anionic surfactants in the formulation (Principles 3, 6, and 10). In addition, the newly developed MWFs are more hard water stable, and this stability is achieved even with the removal of two components found in traditional MWFs that contribute to emulsion stability: ethylenediaminetetraacetic acid (EDTA), a chelating agent, and butyl carbitol, a coupler. By eliminating two components from the formulation, the overall life cycle environmental impact is likely to be reduced (Principle 9). In addition, there are environmental concerns specific to the disposal of EDTA that are eliminated through the development of EDTA-free MWFs such as those described in this paper. For example, EDTA does not readily biodegrade (*8*), and once introduced into the general environment, it can remobilize heavy metals (e.g., zinc and lead) from sediments (*9*) or aquifer material (*10*) allowing metals to re-enter and re-circulate in the food chain. Also, EDTA can mobilize heavy metals in tool coatings, providing a route for these metals to enter the environment. For these reasons, the removal of EDTA from MWF formulations would serve well toward the design of greener metalworking fluids.

Before MWF formulations based on these design strategies can be realized, a fundamental knowledge of component functionality, emulsion stability, and MWF properties must be developed. To date, fundamental research directed toward quantifying these relationships has been limited. While there is copious anecdotal evidence and industry folklore surrounding optimum component selection for MWF longevity, these relationships have not been quantified or are not available in the public domain. Therefore, this research has aimed to correlate MWF component properties with total formulation performance in order to provide the knowledge necessary to design MWF formulations for longevity under anticipated field conditions (e.g., high concentrations of hard water salts). This will lead to a reduction in environmental

hazards and economic costs associated with the acquisition and disposal of MWFs.

The specific objective of this research is to investigate the relationship between emulsifier system properties and MWF stability under hard water conditions for novel MWF formulations based on both petroleum and vegetable oils. Emulsifier properties evaluated include hydrophile:lipophile balance (HLB), hydrocarbon chain length and branching, headgroup charge, chain length, and branching. Other factors evaluated include the molar ratios of emulsifier components and the ratio of total emulsifier to oil. In addition, novel MWF formulations were developed during this research that utilize twin-headed anionic surfactants that have been previously shown to be more resistant to precipitation induced by hard water ions (11) and that can extend the life of traditional MWF formulations. These formulations were evaluated for stability in the presence and absence of EDTA and a commonly utilized coupler component (butyl carbitol) under hard water conditions. The novel formulations were also rigorously evaluated for field performance in manufacturing applications since green engineering necessitates performance that is competitive if not better than the currently available technology.

Metalworking Formulation Background and Theory

Four types of MWFs have been used in practice to accommodate the severity differences between various machining operations: straight oils, oil-in-water emulsions (soluble oils, semi-synthetics), and true solutions (synthetics). The emulsifiable MWFs are defined by the ratio of water to oil in the concentrate, which is related to the amount of lubrication versus cooling that the MWF can provide. For the emulsifiable MWFs, the concentrate is usually diluted 80−95% in water when in use. Given that semi-synthetics account for approximately 40% of the market (1), with continuing increases in market share expected (12), this research investigation focuses on the formulation and performance of semi-synthetic MWFs.

Semi-synthetic MWF formulations include water, oil, and an emulsifier system (e.g., anionic surfactant, nonionic surfactant, and coupler). While emulsifier selection for the specific application of MWF systems has been rarely discussed in the literature, there has been much research into the development of stable emulsions for other applications including foodstuffs, pharmaceuticals, cosmetics, detergents, and cleaning agents (13−16). Emulsifying agents act to lower interfacial tension, thereby allowing the formation of smaller oil-in-water droplets with the same energy input. Emulsifiers also deter or retard droplet coalescence and flocculation by forming an interfacial film around the dispersed-phase droplets to prevent particle interaction (17). The most common means to stabilize emulsion droplets is to employ repulsive electrical or steric forces to retard coalescence (17). When two emulsion droplets bearing the same electric charge approach each other, the charges give rise to a repulsive force between the particles, thereby maintaining discrete and stable emulsion particles (16, 18). Steric interactions occur when the droplets (henceforth referred to as "particles") have layers of surfactant molecules at their water interface. Steric stabilization is especially important for nonionic surfactants, where surfactant molecules may take different orientations leading to "packing effects" that can prevent coalescence and flocculation (19).

A wide range of surfactant properties and types may be used to form and stabilize emulsions. The three broad categories of surfactants that can be considered are nonionic, anionic, and cationic. Cationic surfactants are not typically used in MWF formulations since they may be lost to metal surfaces that are negatively charged at the elevated pH (e.g., 8−10) of MWFs. Nonionic surfactants are electrically neutral

and therefore have the advantage of being relatively unaffected by the hard water ion content of the MWF aqueous phase (20). While anionic surfactants are much more sensitive to hard water, they have the advantage of being more effective at reducing the oil/water interfacial tension for better wetting of the MWF on the metal surface (20). They are also less expensive when compared with nonionic surfactants (21) and are more amenable to waste treatment via emulsion splitting.

Because of their complimentary performance characteristics, the use of a binary mixture of nonionic and anionic surfactants as a synergistic emulsifier system is common in practical applications (22). In the design of these mixtures, it is necessary to establish a balance between anionic surfactants that minimize cost and increase waste treatability and nonionic surfactants that improve hard water and salinity tolerances (23, 24). Mixed emulsifier systems also act to increase the packing density of the surfactant film around the droplet, thus providing improved emulsion stability (25). Although anionic−nonionic surfactant mixtures are universally applied in the metalworking industry, they are not well understood at a fundamental molecular level (26).

In this investigation, MWF formulation stability is evaluated in the presence of the accumulation of dissolved hard water salts. Such an investigation is necessary since concentrations of hard water salts in MWFs can vary significantly under typical manufacturing conditions. Hard water salts are introduced into the system when tap water is added to replenish water lost due to evaporation. The amount of water lost from a typical 100 000-gal system can exceed 100 gal/d, leading to regular additions of large amounts of tap water. After 40 d in the field, hard water salt concentrations have been measured as high as 1000 ppm (27). Increasing concentrations of these salts have been shown to have a significant and adverse impact on emulsion particle size stability. For instance, while increasing emulsion particle size can lead to slight improvements in machining performance, it can result in emulsion and microbial instability (28, 29). Previous tests on a commercial MWF indicated that a particle size shift from 20 to 2000 nm resulted in a 440% increase in microbial load during a 48-h inoculation (28). Increased microbial growth can lead to the release of acids, which can lower pH, and further increase particle size. Both microbial and emulsion instabilities can ultimately lead to oil−water phase separation, causing large reductions in lubricity, increases in tool breakage, and more frequent MWF disposals, leading to significant environmental impact. For these reasons, a chelating agent such as EDTA is commonly included in MWF formulations. EDTA prevents disruption of electrostatic forces (28) that stabilize emulsion particles by complexing with hard water ions. However, EDTA can be ineffective in maintaining emulsion stability under hard water conditions (28). Ideally, these formulations designed for improved lifetime under hard water conditions would not rely on EDTA, as EDTA can be only marginally effective and has its own environmental impacts.

Experimental Materials and Methods

The MWF formulations described in this paper were based on a generic recipe for semi-synthetic MWF concentrates provided by a commercial MWF supplier as shown in Table 1. Modified concentrates based on this formulation were diluted to 5 wt % in deionized water for all MWF property characterization and machining evaluations performed during this research. Each formulation was identical in all components and concentrations except for the oil and surfactant system. While total molar surfactant concentration was held constant throughout the experiments, the anionic: nonionic surfactant ratio was varied according to a gradient scheme. The molar concentration of anionic surfactant was

TABLE 1. Recipe for Baseline Semi-synthetic Metalworking Fluid

component	molar concn in concentrate	molar concn in use (5% dilution)
water (deionized)		
coupler (butyl carbitol)	9.3×10^{-2}	4.6×10^{-3}
tall oil fatty acid (<20% rosin)	1.3×10^{-1}	6.6×10^{-3}
corrosion inhibitor (monoethanolamine borate)	1.3	6.4×10^{-2}
oil (mineral or vegetable)	3.8×10^{-1}	1.9×10^{-2}
anionic (petroleum- or bio-based)	1.3×10^{-1}	6.6×10^{-3}
nonionic (petroleum- or bio-based)	6.0×10^{-1}	3.0×10^{-2}

varied by 25%, 50%, 75%, 100%, and 200% of the base concentration listed in Table 1, with the nonionic surfactant making up the balance to maintain a constant total surfactant molar concentration. Similarly, the molar concentration of oil was varied between 33%, 67%, 100%, 133%, and 200% of the base concentration listed in Table 1, while again maintaining a constant total surfactant molar concentration. All of the fluid components were used as delivered from the manufacturer and were subject to the same handling and storage conditions. In addition, two commercially available semi-synthetic MWFs (SS1 and SS2) produced by different, large market-share manufacturers were used as benchmarks to compare with the novel formulations developed during this investigation. Both SS1 and SS2 featured a naphthenic mineral oil base and an emulsifier system of anionic sodium petroleum sulfonate (SPS) and nonionic di-2-propanol amine in molar concentrations and ratios similar to those listed in Table 1.

Materials. All of the fluid formulations developed for this research were comprised of identical concentrations of deionized water, butyl carbitol (coupler), tall oil fatty acid (less than 20% rosin), and monoethanolamine borate (corrosion inhibitor) as shown in Table 1. The base oils used in the formulations were a petroleum-based naphthenic oil and a bio-based high oleic canola oil that was modified for oxidative stability (AgriPure 900, Cargill Inc., Minneapolis, MN) as shown in Table 2. Combinations of four anionic and 12 nonionic surfactants were evaluated as emulsifier systems to cover a large range of HLB and structural properties (e.g., branched tail, branched head, straight chain). HLB represents the ratio of surfactant hydrophilicity (e.g., size/structure of polar headgroup) to lipophilicity (e.g., size/structure of nonpolar tail group). The HLB requirements for stable oil-in-water (o/w) emulsions have been reported to be 12 for aromatic mineral oils and 7−12 for vegetable oils (30). All anionic and nonionic surfactants investigated were commercially available and petroleum based. However, it is known that the linear alcohol ethoxylate nonionic surfactants can be manufactured from bio-based feedstocks such as palm kernel oil or coconut oil. In all cases the surfactants were composed of a distributed mixture. Consequently, the molecular structures and chain lengths shown in Table 2 represent average properties as reported by the manufacturer.

MWF Property Characterization. MWF emulsion properties that were directly measured include particle size, contact angle, surface tension, and tramp oil rejection. In some cases, concentrates were further evaluated by absorbance and viscosity measurements. Particle size was evaluated using photon correlation spectroscopy (PCS), which allows for the detection of subtle emulsion particle size changes, including indications of coalescence (17, 31). For

this research, a Nicomp 370/DLS (Particle Sizing Systems, Santa Barbara, CA) particle sizing system was used, with its particle size estimation capability verified independently by a wide-angle laser light scattering apparatus similar to the one described by Lee et al. (32). For characterization results reported here, three aliquots from each formulation were analyzed by PCS and averaged. Distributions were compared by the χ^2 test, with the particle size distribution at 0 ppm hardness used as the reference distribution. A confidence level of 90% was used to determine statistical significance.

The new MWF designs were evaluated and compared with SS1 and SS2 for performance metrics including contaminant oil rejection, contact angle, and lubricity. To evaluate contaminant oil rejection, a fixed amount of dyed paraffinic mineral oil was added to the diluted metalworking fluid. The system was then vigorously mixed. The time to separation was determined when 95% of the volume of added paraffinic oil had separated. Contaminant oil was simulated using paraffinic mineral oil dyed with Oil Red O (Fisher Scientific International, Pittsburgh, PA).
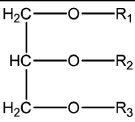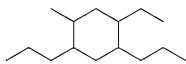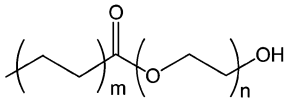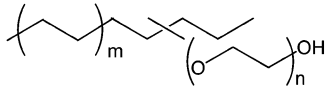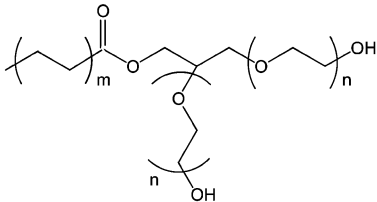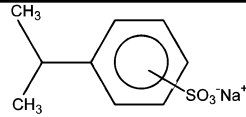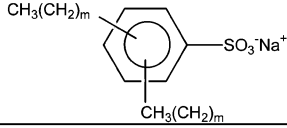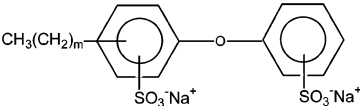
Contact angle, a measure of MWF wettability, was measured by methods similar to those described in Demond et al. (33) using an axisymmetric drop shape analysis (ADSA) apparatus. In this technique, a syringe was used to form a drop of the MWF on a sample of 1018 cold rolled steel, which was the metal used for tapping torque validation experiments. The droplet was then magnified using a M3Z Plan S microscope (Wild Letz, Heerbrugg, Switzerland) and photographed using a CCD monochrome camera (4810 series, Coho, San Diego, CA). Surface tension was measured using a DuNouy ring tensiometer (Kruss USA, Charlotte, NC).

Machining performance of the MWFs developed during this research was measured for the fluids by the tapping torque test. Tapping is a metalworking operation in which threads are cut or formed inside a predrilled hole by tools called taps. When cutting threads with a tap, high metal removal rates are expected, and large forces develop due to the friction between the tool and the workpiece (33). Under these conditions, MWF becomes particularly important; therefore, tapping torque performance is widely used as a standard measure of MWF quality (34). The tapping torque test has been gaining wide acceptance as a means of MWF evaluation because it fulfills a number of desired testing requirements: (a) correlation with field results, (b) simplicity, (c) speed, (d) economy, (e) small test samples, (f) precision, and (g) severe conditions.

For validation experiments, a MicroTap Mega G8 (Rochester Hills, MI) tapping machine tool was utilized at a machining speed of 1000 rpm to cut threads into 1018 cold rolled steel workpieces that were pre-drilled and pre-reamed with 240 M6 holes (Maras Tool, Schaumburg, IL). Uncoated high-speed steel taps with 60° pitch and 3 straight flutes were used for the machining operation. MWF evaluations were carried out according to ASTM D 5619, the Standard for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine (35) with several modifications made to account for the use of a MWF evaluation testbed that permits multiple evaluations on a single workpiece as proposed by Zimmerman et al. (36). MWF performance is reported here as tapping torque efficiency (η), where higher efficiency indicates improved performance in the tapping torque test. It has been demonstrated that a correlation exists between high tapping torque efficiency, long tool life, good surface integrity of the thread, and an effective metalworking fluid (35).

MWF Stability Testing. The concentrate and diluent of each MWF formulation was first tested for emulsion stability by a visual evaluation of concentrate and diluent stability as described by Kipers et al. (37). Then each visually stable formulation was subjected to particle size measurement via

TABLE 2. Oil, Anionic Surfactant, and Nonionic Surfactant Structures and Properties Considered during the Present Investigation [f]

oil	oil class	chemical structure	viscosity (40 °C cSts)	density (g/mL)
Cargill AP 900 (modified Canola oil)	bio-based	chemical composition of canola oil (Fatty Acid Profile in mole %) 16:0 16:1 18:0 18:1 18:2 18:3 20:0 20:1 22:0 22:1 R1 4.1 0.3 2.2 23.1 11.1 6.4 - 16.4 1.4 34.9 R2 0.6 0.2 - 37.3 36.1 20.3 - 2.0 - 3.3 R3 4.3 0.3 3.0 16.6 4.0 2.6 - 17.3 1.2 51.0	39.93	0.91
mineral oil (naphthenic)	petroleum-based		65.56	0.9

nonionic surfactant	surfactant class	chemical structure	m	N	Avg. MW	HLB
Tomadol 23-1 Tomadol 23-3 Tomadol 23-6.5 Tomadol 1-3 Tomadol 1-7 Tomadol 91-3 Tomadol 91-6	primary (linear) alcohol ethoxylate		12,13 12,13 12,13 11 11 9,10 9,10	1 3 6.5 3 7 3 6	238[a] 322[a] 484[a] 305[a] 479[a] 281[a] 425[a]	3.7[a] 7.9[a] 12[a] 8.7[a] 12.9[a] 8.5[a] 12.4[a]
Tergitol 15-S-3 Tergitol 15-S-5 Tergitol 15-S-7	secondary alcohol ethoxylate		12-14 12-14 12-14	3 5 7	332[b] 420[b] 508[b]	8[b] 10.5[b] 12.1[b]
Tagat V 15 Tagat V 20	ethoxylated glyceryl ester		12 12	15 20	2200 2500	7.0[c] 8.4[c]

anionic surfactant	surfactant class	chemical structure	m	n	Avg. MW	HLB
sodium cumene sulfonate (SCS)	alkylbenzene sulfonate		-	-	222[d]	13.7[e]
sodium xylene sulfonate (SXS) sodium petroleum sulfonate (SPS)	sodium dialkyl sulfonate		0 ~4.5	- -	208[d] 455[d]	14.2[e] 6.6[e]
Dowfax 3B2 (D3B2)	alkyldiphenyl oxide disulfonate		10	-	542[b]	25.6[e]

[a] As reported by Tomah Incorporated. [b] As reported by Dow Chemical Company (*42*). [c] As reported by Degussa AG. [d] As reported by Stepan Company. [e] As calculated by the additivity principle as reported by Davies (*43*) and Becher (*44*). [f] The surfactant structures shown represent the average properties of the commercially available distributed surfactant mixtures as reported by their respective manufacturers.

photon correlation spectroscopy at varying levels of hard water ion concentration. Initially, the concentrate was formulated, vigorously shaken, allowed to sit for 7 d, and evaluated. Next, the concentrate was diluted to 5% in deionized water, vigorously shaken, allowed to sit for 7 d, and evaluated. Finally, the concentrate was diluted in increasing concentra- tions of hard water from 0 to 1000 ppm as CaCO$_3$ and allowed to sit for 7 d. If layers or precipitates were found in a formulation upon examination at any stage of stability testing, it was not subjected to further evaluation. Concentrates and diluents were reevaluated for stability after 3 months and in some cases after 6 months. Each formulation was generated
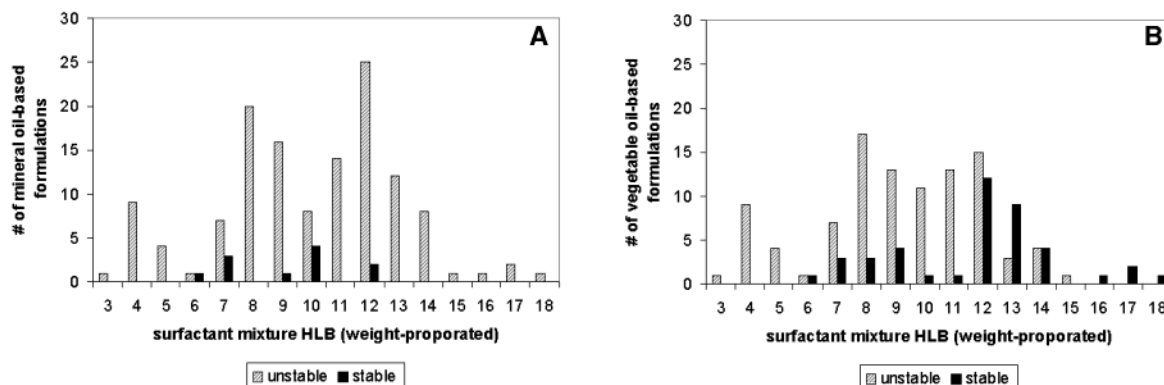
FIGURE 1. Number of stable (A) mineral oil- and (B) vegetable oil-based concentrate formulations vs surfactant mixture HLB (weight-proportioned); 140 formulations shown in each figure.
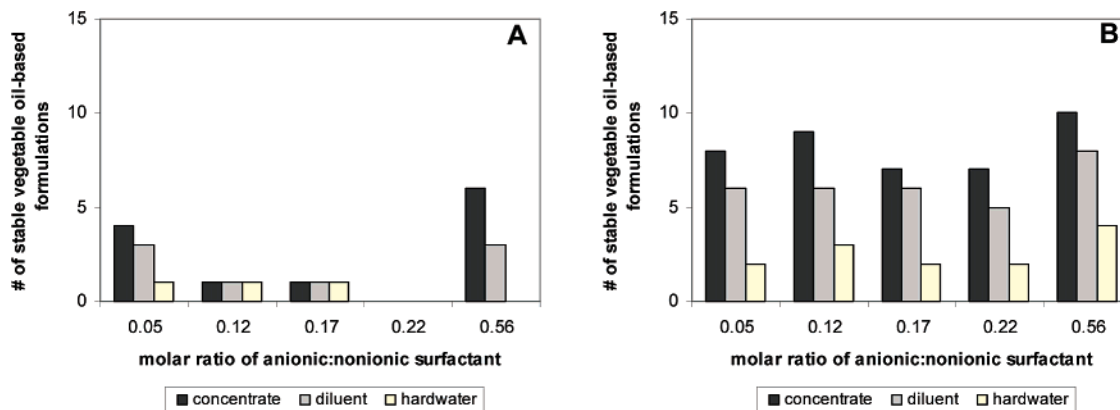

FIGURE 2. Number of (A) mineral oil- and (B) vegetable oil-based stable concentrates, stable diluents, and hard water stable diluents as a function of anionic:nonionic surfactant molar ratio; 140 formulations shown in each figure.

in triplicate, and each property was characterized with three samples from each formulation.

Results and Discussion

Impact of HLB and Anionic:Nonionic Molar Ratio on MWF Stability. The impact of hydrophile:lipophile balance on MWF formulation stability was evaluated for the two base oils listed in Table 2. The 280 potential MWF formulations were developed using each of the anionic surfactants described in Table 2 and the nonionic surfactant Tomadol 23-1 at the gradients specified in section 2 to cover a wide range of HLB values. For this research, the HLB of the emulsifier system was calculated on a weight-proportioned basis as prescribed by Adamson and Gast (*25*). Figure 1 indicates that the Cargill AP900 canola oil can form stable MWF formulations over a much greater HLB range than naphthenic mineral oil for the surfactants and concentrations investigated. While vegetable oil-based concentrate formulations were stable over an HLB range from approximately 6 to 18, stable mineral oil-based concentrate formulations were only generated in a range from 6 to 12.

It is commonly assumed that once an optimum HLB is found, any other mixture of surfactants with that HLB will also be at its optimum HLB (*25*). Since this simple method of choosing emulsifiers has proven to be ineffective for complex emulsion systems, MWF formulators often rely on anecdotal knowledge of emulsifier behavior to successfully choose the best emulsifier for a given system (*17*). Consistent with experience in the industry, Figure 1 suggests that a single indicator of surfactant properties such as HLB is not predictive in the preparation of stable MWF formulations. At a certain HLB value, both stable and unstable formulations were observed. This suggests that other physical characteristics,

such as head and tail group surfactant structures, should be considered when trying to predict the stability of an emulsifier system during the design of MWF formulations.

In addition to evaluating surfactant HLB values for emulsion stability, the molar ratio of anionic to nonionic surfactant was varied over 1 order of magnitude from 0.05 to 0.56. The total molar concentration of surfactant was held constant, and only the ratio of anionic to nonionic surfactant was varied. The results shown in Figure 2 indicate that the molar ratio of the anionic to nonionic surfactant has little impact on the stability of the concentrate or the diluent regardless of the base oil selected.

Impact of Anionic and Nonionic Emulsifier Characteristics on MWF Stability. To investigate the impacts of anionic and nonionic structural characteristics on the design of stable MWF formulations, an emulsifier system was generated for each nonionic and anionic surfactant combination (4 anionic, 12 nonionic surfactants) listed in Table 2. This resulted in 48 emulsifier system combinations to be investigated for both the mineral oil- and vegetable oil-based MWFs. The three anionic and three nonionic surfactant classes shown in Table 2 were selected to be representative of twin-headed, twin-tailed, and straight chain structures. Sodium petroleum sulfonate (SPS), which is the anionic emulsifier traditionally used in MWFs, was also evaluated in these systems as a reference case. Formulations were generated by adding the nonionic at 25%, 50%, 75%, 100%, and 200% of the base concentration listed in Table 1. A balance of anionic surfactant was added to maintain a constant total surfactant molar ratio.

Figure 3 provides a summary of the 480 formulations (12 nonionics × 4 anionics × 5 molar ratios × 2 base oils = 480 formulations) generated during these experiments. The results for the mineral oil-based formulations (Figure 3A)

A

tail length \ head length	1 (straight)	3 (straight)	5 (straight)	~6.5 (straight)	15 (branched)	20 (branched)
9,10 (straight)		◐ ▦		◐ ▮		
11 (straight)		◑ ▮		○		
12,13 (straight)	◑ ▦	○		◑ ▦	○	○
12-14 (branched)		○	○	○		

B

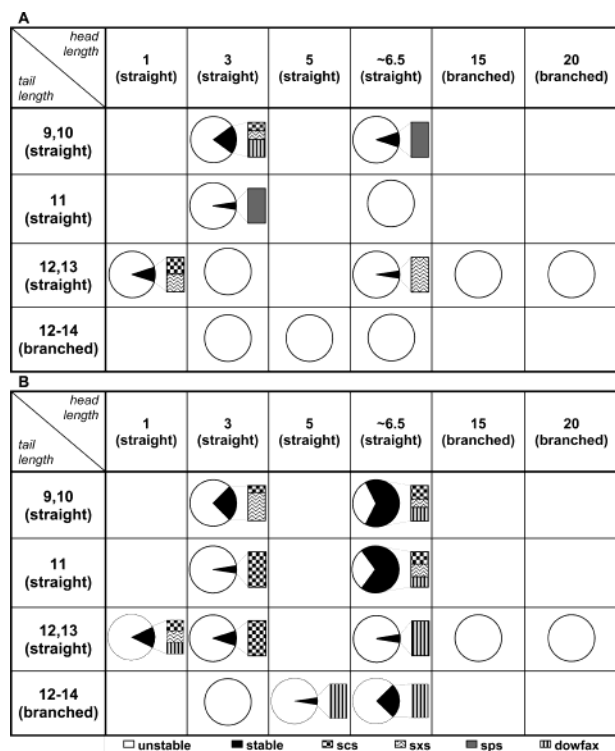| tail length \ head length	1 (straight)	3 (straight)	5 (straight)	~6.5 (straight)	15 (branched)	20 (branched)
9,10 (straight)		◕ ▦		◔ ▦		
11 (straight)		◑ ▦		◔ ▦		
12,13 (straight)	◑ ▦	◑ ▦		◑ ▮	○	○
12-14 (branched)		◑ ▮		◔ ▮		

☐ unstable ■ stable ▩ scs ▧ sxs ▮ sps ▥ dowfax

FIGURE 3. Number of stable (A) mineral oil- and (B) vegetable oil-based concentrates and diluents as a function of nonionic surfactant head and tail structure properties and anionic surfactant. Each cell represents 20 formulations. (Legend abbreviations refer to anionic surfactants listed in Table 2.)

indicate that 11 of the emulsifier system combinations yielded stable concentrates and diluents. Additionally, each of the anionic surfactants resulted in at least one stable concentrate and diluent. However, none of the secondary alcohol ethoxylates (branched tail) or ethoxylated glyceryl ester (branched head) nonionic surfactants resulted in a stable mineral oil-based formulation, regardless of the anionic surfactant in the mixture. On the basis of these surfactant combinations, a shorter nonionic surfactant tail length appears to increase the likelihood of achieving a stable mineral oil-based formulation.

The results for the vegetable oil-based formulations (Figure 3B) indicate that 31 of the emulsifier system combinations yielded stable concentrates and diluents. However, all the formulations with SPS were unstable regardless of the nonionic surfactant selected. Similar to the mineral oil-based formulations, the ethoxylated glyceryl ester (branched head) nonionic surfactants did not result in any stable vegetable oil-based formulations. Experimental results for these 240 formulations suggest that a nonionic ethylene oxide chain headgroup length of ~6.5 increases the likelihood of a stable vegetable oil-based MWF formulation.

To better understand the relationships between anionic and nonionic surfactant characteristics, a numerical correlation analysis was performed that was based on the results presented in Figure 3. The correlation factors listed in Table 3 represent the covariance of the nonionic surfactant head and tail length (i.e., the percent of stable formulations divided by the product of standard deviations). The results indicate that there is a strong correlation (0.75) between nonionic surfactant headgroup and a stable vegetable oil-based MWF formulation. This correlation was not observed in mineral oil-based formulations. The data also indicate a slight correlation (−0.33) between nonionic surfactant tail lengths and achieving a stable mineral oil-based formulation.

TABLE 3. Correlation between Nonionic Surfactant Properties and Stable Mineral Oil- and Vegetable Oil-Based Metalworking Fluid Formulations for the Anionic Surfactants Listed in Table 2

	mineral oil base			vegetable oil base		
	tail	head	stable formulation	tail	head	stable formulation
tail	1			1		
head	na[a]	1		na[a]	1	
stable formulation	−0.33	0.16	1	−0.22	0.75	1

[a] na, not applicable.

Impact of Anionic and Nonionic Emulsifier Characteristics on Particle Size Stability in Hard Water Conditions. The concentrate dilutions found to be stable in Figure 3 were then evaluated for particle size shifts in 300 and 800 ppm calcium chloride. For the purposes of this analysis, particle size stability under hard water conditions was operationally defined as a statistically unobservable particle size shift over the range from 0 to 800 ppm hardness. The results from these hard water experiments indicate that by this definition *only* the twin-headed anionic surfactant (D3B2) yields stable formulations. Specifically, this twin-headed anionic surfactant yielded 17 vegetable oil- and 3 mineral-oil based formulations with stable emulsion particle sizes in hard water conditions. The oil and emulsifier system components, and their respective concentrations, for these 20 hard water stable formulations are listed in Table 4. In most cases, slight increases in hard water concentration (300 ppm) caused an increase in particle size. However, as hard water ion concentration increased up to 800 ppm, the particle size was found to shift back into the initial particle size range.

To further explore this phenomenon, the hard water (calcium) concentration was evaluated at 0, 100, 200, 300, 500, 750, and 1000 ppm as $CaCO_3$, with particle size measurements taken after 7 d. At low hard water concentrations of 100 and 200 ppm, slight increases in particle size were observed. At 300 ppm hardness as $CaCO_3$, the particle size increased to its maximum, suggesting that the emulsions are flocculating as the calcium binds to the anionic headgroups exposed at the water−oil emulsion interface, disrupting the electrostatic repulsive forces. However, as hard water is incrementally increased from 300 to 1000 ppm, it was found that the particle size incrementally *decreases*. At 1000 ppm calcium concentration, the particle size was measured to be statistically identical to the fluid with no calcium added. This decrease of particle size at high calcium concentrations appears to be due to the existence of soluble anionic surfactant−cation complexes at high cation concentrations as reported by Talens-Alesson (*38*), Tezak et al. (*39*), and Fisher and Oakenfull (*40*).

Contrary to these observations with novel MWFs based on D3B2, the results shown in Figure 4 demonstrate that when calcium was introduced to SS1 and SS2 there is a trend of increasing particle size with increasing calcium concentration. In fact, when 0.008 M of calcium chloride was introduced to SS2, the MWF split into separate oil and water phases despite the presence of EDTA.

In addition to increased hard water stability, which will increase in-service lifetime of the MWF, there is other evidence to suggest that these formulations based on D3B2 have less environmental impact. For instance, the newly developed MWFs based on D3B2 as the anionic surfactant are formulated without EDTA, which is known to be of environmental concern as described previously. Moreover, D3B2-based emulsifier systems may be less toxic than emulsifier systems based on SPS. This is based on data for

TABLE 4. Oil and Emulsifier System Components and Concentrations for Novel Semi-synthetic Metalworking Fluid Formuations Demonstrating Particle Size Stability in Hard Water Conditions

|	oil base	molar concn in 5% dilution	anionic surfactant	molar concn in 5% dilution	nonionic surfactant	molar concn in 5% dilution	HLB
V1	AP900 (canola)	0.019	D3B2	0.013	Tomadol 23-1	0.023	11.6
V2	AP900 (canola)	0.019	D3B2	0.0013	Tomadol 23-6.5	0.023	16.9
V3	AP900 (canola)	0.019	D3B2	0.0016	Tomadol 1-7	0.035	13.5
V4	AP900 (canola)	0.019	D3B2	0.0040	Tomadol 1-7	0.033	14.3
V5	AP900 (canola)	0.019	D3B2	0.0053	Tomadol 1-7	0.031	15.2
V6	AP900 (canola)	0.019	D3B2	0.013	Tomadol 1-7	0.023	17.5
V7	AP900 (canola)	0.019	D3B2	0.0016	Tomadol 91-6	0.035	13.0
V8	AP900 (canola)	0.019	D3B2	0.0040	Tomadol 91-6	0.033	13.8
V9	AP900 (canola)	0.019	D3B2	0.0053	Tomadol 91-6	0.031	14.3
V10	AP900 (canola)	0.019	D3B2	0.0066	Tomadol 91-6	0.030	14.8
V11	AP900 (canola)	0.019	D3B2	0.013	Tomadol 91-6	0.023	17.2
V12	AP900 (canola)	0.019	D3B2	0.013	Tergitol 15-S-5	0.023	15.9
V13	AP900 (canola)	0.019	D3B2	0.0016	Tergitol 15-S-7	0.035	12.7
V14	AP900 (canola)	0.019	D3B2	0.0040	Tergitol 15-S-7	0.033	13.6
V15	AP900 (canola)	0.019	D3B2	0.0053	Tergitol 15-S-7	0.031	14.0
V16	AP900 (canola)	0.019	D3B2	0.0066	Tergitol 15-S-7	0.030	14.5
V17	AP900 (canola)	0.019	D3B2	0.013	Tergitol 15-S-7	0.023	17.0
M1	mineral (naphthenic)	0.019	D3B2	0.0017	Tomadol 91-2.5	0.035	9.3
M2	mineral (naphthenic)	0.019	D3B2	0.0040	Tomadol 91-2.5	0.040	10.3
M3	mineral (naphthenic)	0.019	D3B2	0.0066	Tomadol 23-1	0.030	7.6
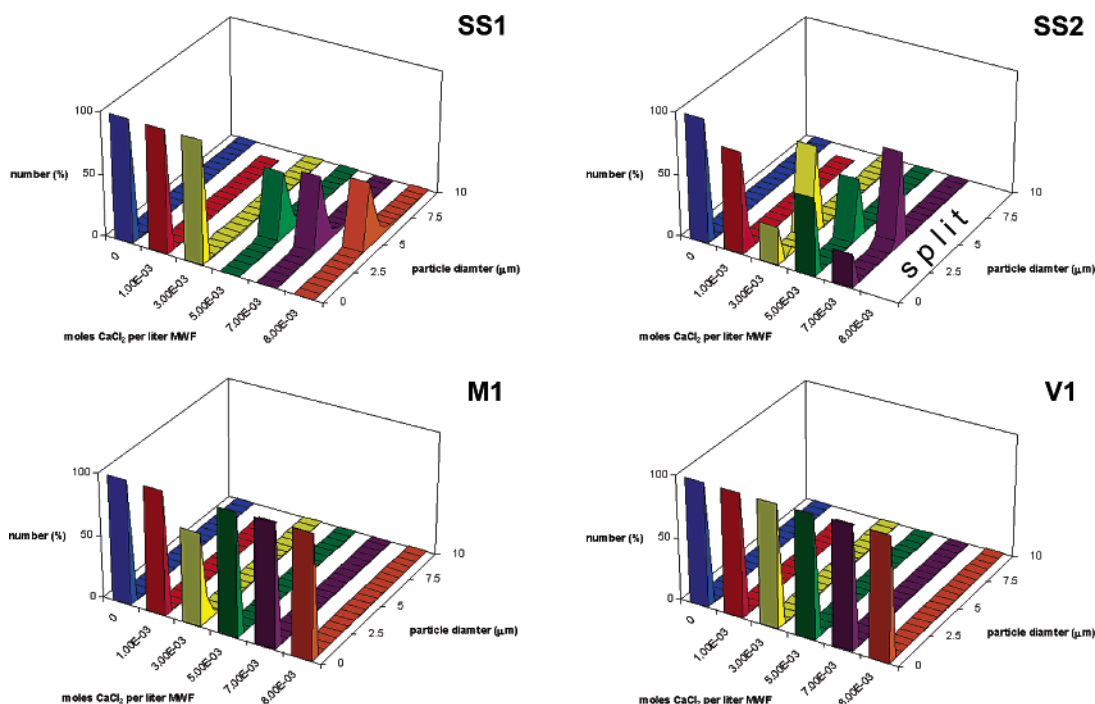
FIGURE 4. Particle size of SS1, SS2, and representative mineral oil- and vegetable oil-based formulations (M1 and V1) formulated with D3B2 as a function of calcium chloride salt molar concentration. For systems where oil–water split occurs, particle size data are not available. Formulations for M1 and V1 can be found in Table 4.

the fathead minnow (*Pimephales promelas*), which indicate that SPS has an LC$_{50}$ of 0.4 mg/L after 48 h while D3B2 has an LC$_{50}$ of 14.1 mg/L after 48 h (*41*).

Impact of Oil:Emulsifier Molar Ratio on Particle Size Stability in Hard Water Conditions. While the molar ratio of anionic to nonionic surfactant in the formulation has little effect on the stability of MWFs, it is necessary to evaluate the molar ratio of the total surfactant system to the base oil since some manufacturing operations require MWFs with a greater oil weight percentage for greater lubricity. For these experiments, the total moles of surfactant in the formulation were held constant while the molar concentration of the oil phase was varied from 6.25×10^{-3} to 3.75×10^{-2} M to cover the definitional range of semi-synthetic MWFs (5–30% oil by

weight) (*1*). More specifically, the molar oil:emulsifier ratio was evaluated at 0.1, 0.3, 0.5, 0.7, and 1.

The results shown in Figure 5 indicate that the initial particle size range (10–25 μm) for each of the 20 formulations increased with increasing oil concentration. This was expected given that a fixed amount of emulsifier provides less available emulsifier to stabilize increasing amounts of oil at the same particle size. A similar trend was also observed at each increment of increasing hardness concentration. Larger initial particle sizes due to increasing oil concentration correlated very well with larger particle sizes at 800 ppm hardness. At an oil:emulsifier molar ratio of approximately 1, the particle size of both the mineral oil- and vegetable oil-based formulations was greater than 1 μm (detection limit
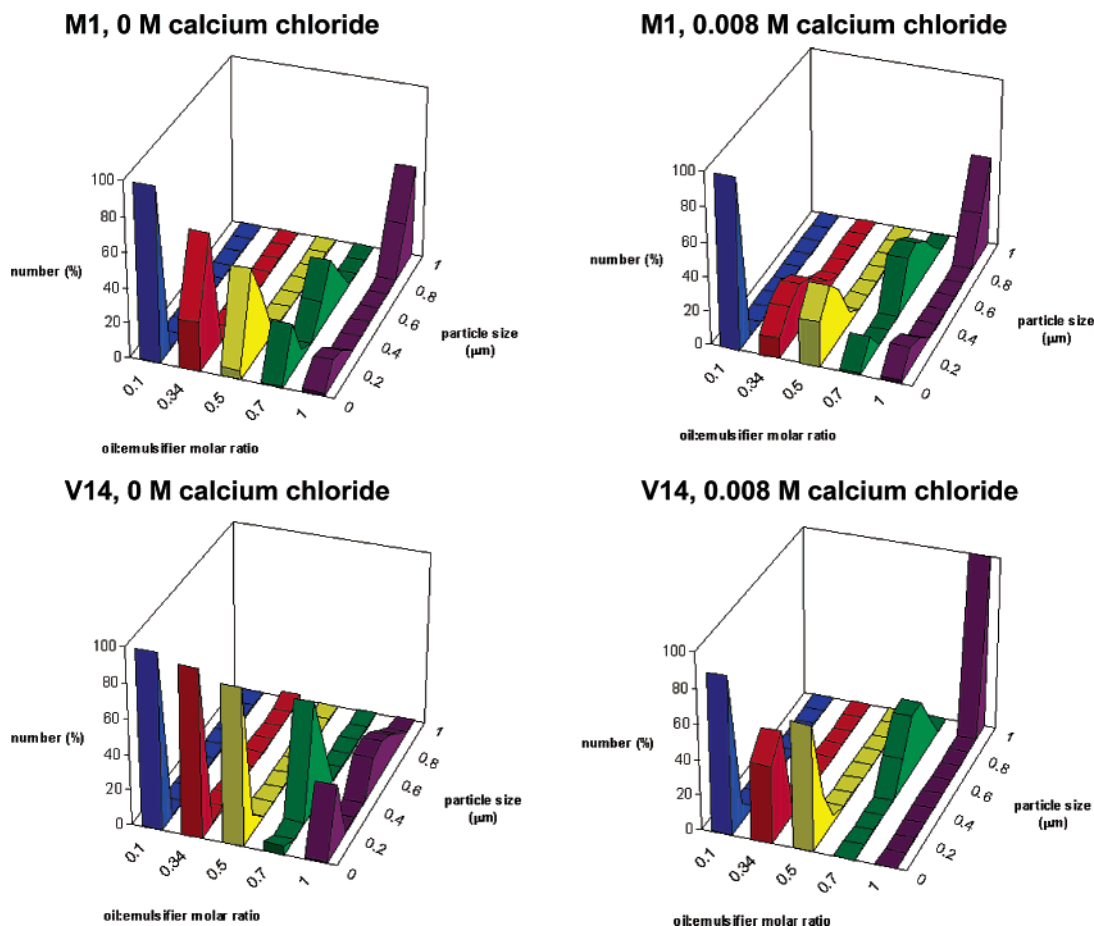
FIGURE 5. Particle size of representative mineral oil- and vegetable oil-based formulations (M1 and V14) as a function of oil:emulsifier molar ratio at 0 and 0.008 M calcium chloride. Data reported for particle size distributitons at 1 μm is at the detection limit of Nicomp 370 PCS particle size system. Formulations for M1 and V14 can be found in Table 4.

of PCS) at 800 ppm hardness. This suggests that a higher emulsifier concentration is necessary to maintain particle size stability in hard water conditions at 30% oil by weight. This was confirmed by (i) doubling the surfactant concentration in the 30% oil formulation to achieve an oil:emulsifier molar ratio of 0.5 and (ii) evaluating the system under hard water conditions. The results showed no statistically significant particle size shift from 0 to 1000 ppm hardness at an oil:emulsifier molar ratio of 0.5. Consequently, these experiments suggest that a MWF formulation should optimally have an oil:emulsifier molar ratio of 0.5 or less for particle size stability in hard water conditions when using D3B2 as the anionic surfactant in the emulsifier system.

Impact of Coupler Concentration on Particle Size Stability in Hard Water Conditions. Couplers are included in MWF formulations to regulate clarity and viscosity and tend to act quickly at the oil−water interface, require no hazard labeling, and be relatively inexpensive (*1*). In this research, the role of a butyl carbitol coupler was investigated in the 17 vegetable oil and 3 mineral oil MWF formulations with demonstrated hard water stability at 1000 ppm hardness as $CaCO_3$. In the case of the mineral oil-based formulations, the removal of the coupler caused the concentrate to become unstable. It was found that a minimum concentration of 5.6 $\times 10^{-2}$ M (60% of the base concentration listed in Table 1) was necessary for the mineral oil-based concentrates to become stable. Upon dilution and further testing, however, this coupler concentration did not provide particle size stability in hard water conditions. Therefore, nearly all of the coupler concentration listed in Table 1 is necessary for hard water stability in the mineral oil-based formulations. How-

ever, in the case of all 17 vegetable oil-based formulations, the removal of the coupler did not have a major affect on the stability of the concentrate or the diluent below 800 ppm hardness as $CaCO_3$.

A comparison of the mean particle size of several representative fluids with and without coupler at 0 and 800 ppm hardness is presented in Figure 6. The results from identical experiments with SS1 are also provided for comparison. Although the vegetable oil-based formulations investigated are somewhat dependent on the coupler for diluent stability in very hard water conditions, they are more stable than SS1 and SS2 with both coupler and EDTA. Therefore it may be possible to remove or reduce the amount of coupler. This would be desirable since this could reduce the overall life cycle environmental impact of the MWF formulation by decreasing the need to acquire, process, and dispose of the coupler component. When considered in conjunction with the results that support the ability to remove EDTA from the bio-based formulations, robust bio-based MWF formulations may be possible that contain fewer environmentally impacting components than traditional MWFs.

Performance Evaluation of Novel MWF Formulations. Developing novel petroleum- and bio-based MWFs with greater stability in hard water requires that these formulations perform as well, if not better than, currently available commercial MWFs. Toward this end, three key performance parameters (tramp oil rejection, contact angle, and machining efficiency) were compared with the commercially available SS1 and SS2 formulations. The results are described in the following paragraphs.
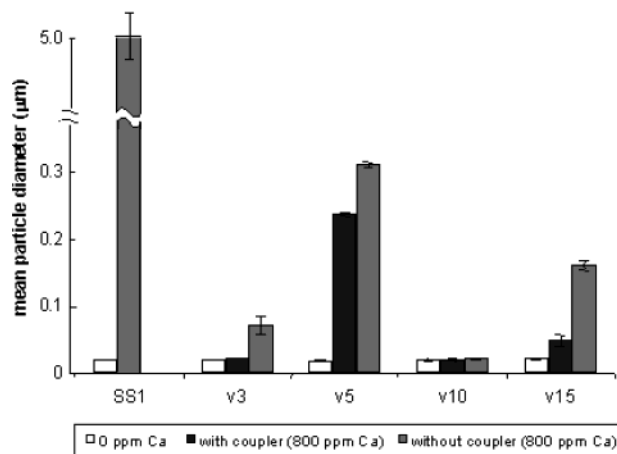
FIGURE 6. Mean particle diameter of commercial formulation SS1 and representative vegetable oil-based formulations (V3, V5, V10, and V15) at 0 ppm calcium chloride and at 0.008 M calcium chloride with and without coupler included in the formulation. Error bars indicate the standard deviation of the average mean particle diameter (triplicate samples).

FIGURE 7. Normalized tramp oil rejection time as function of HLB for all mineral oil- (M1—M3) and vegetable oil-based (V1—V17) formulations that demonstrated hard water stability at 800 ppm calcium. SS1 and SS2 are shown for comparison.

Tramp Oil Rejection. The incorporation of contaminant oil into the MWF system can occur due to hydraulic leaks, way or gear lube leaks, or leaks from forced lubrication systems. If these "tramp" oils become emulsified into the MWF, they can increase the size of the emulsion leading to microbial instability and oil/water phase separation. The emulsification of tramp oil can also directly affect the particle size stability in a manner similar to the particle size increase observed when the oil:emulsifier ratio increases above 0.5 by increasing the amount of emulsifiable oil present in the system. Therefore, the MWFs developed in this investigation were designed to "reject" tramp oil. Since the rejected oil is not emulsified and is less dense than water, it will float on top of the MWF for easy removal from the system.

As listed in Table 4, 20 of the 2500 MWF emulsifier systems exhibited particle size stability in severely hard water conditions and therefore serve as candidates for novel, environmentally improved MWF formulations. Each of the 20 formulations was evaluated for tramp oil rejection and compared with SS1 and SS2. The results indicate that the time for complete tramp oil rejection is slower on average for the new vegetable oil-based formulations and about equal for the mineral oil-based formulations (Figure 7). This probably corresponds with the fact that a paraffinic oil (hydraulic oil), similar to AP900, requires a higher emulsifier system HLB for solubilization. The AP900 fluids are formulated at higher HLB values (11.6—17.5), which may be closer to the HLB necessary to emulsify paraffinic oil. This could consequently lead to slower separation times as the emulsion is more hospitable to the paraffinic oil found for the lower HLB mineral oil emulsion systems (7.6—10.3). Although slower, the tramp oil rejection time of the vegetable base oils is still competitive with commercial MWFs, as the average rejection time is 40 s versus 20 s for the mineral oil-based systems including SS1 and SS2. This difference is not expected to be a problem in practice based on the significant residence time of MWFs in holding tanks during service in actual manufacturing applications.

Contact Angle. In the metal cutting process, MWFs provide boundary lubrication at the point where the tool is in contact with the workpiece. This type of lubrication is directly impacted by the ability of a MWF to coat or "wet" the metal surface. One measure of coating ability is contact angle. As the contact angle decreases, the fluid better wets the surface and increases the probability that the lubricant will reach
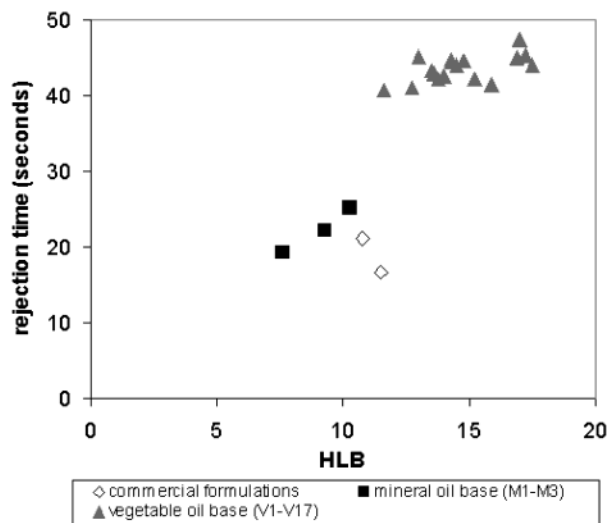
where it is needed. Additionally, wetting may be an important parameter in the delivery of specialty components such as extreme pressure (EP) additives. EP additives, typically containing sulfur, chlorine, and phosphorus, provide necessary lubrication under severe (e.g., high pressure, low speed, minimal clearance) machining conditions. To be effective, EP additives must dissolve in the MWF formulation and reach the appropriate surfaces during the cutting process. It is therefore believed that the more wetting the fluid, the more likely EP additives are delivered to the surface where they are needed (*1*).

As shown in Figure 8, water has a contact angle close to 90° and tends not to wet 1018 cold rolled steel (a typical workpiece material in the fabricated metal products industry). For the same alloy of steel, both SS1 and SS2 demonstrate a lower contact angle, between 30° and 45°, and will tend to spread only slightly. In contrast, the formulations developed during this research (such as M3, V1, and V7) have an even lower contact angle (less than 15°), indicating that they better wet the steel surface.

Machining. The machining performance evaluation shown in Figure 9 suggests that all of the novel MWFs developed during this research are also competitive with traditional semi-synthetic MWF formulations with respect to tapping torque performance. In fact, all of the newly developed formulations demonstrated an equal or higher machining efficiency than SS1 and SS2 prior to the addition of hard water. Interestingly, the tapping torque efficiency measurements indicate that the newly developed bio-based MWF formulations had a slightly lower machining efficiency than the newly developed petroleum-based formulations (Figure 9). For both the petroleum and the bio-MWFs, there was no observable trend when hard water was introduced. At 0 ppm hard water, all of the new formulations had a higher machining efficiency than SS1 or SS2. At other hard water conditions, the new formulations had an indistinguishable or lower machining efficiency than SS1 and SS2. It is interesting to note that the same base mineral oil provided higher machining efficiency with the new emulsifier system (M1, M2, and M3) than it did with the traditional emulsifier system based on SPS and di-2-propanol amine (SS1 and SS2). This may be the result of D3B2 supplying twice as many moles of sulfur, a known EP additive, per mole of surfactant than SPS due to the twin-headed structure.
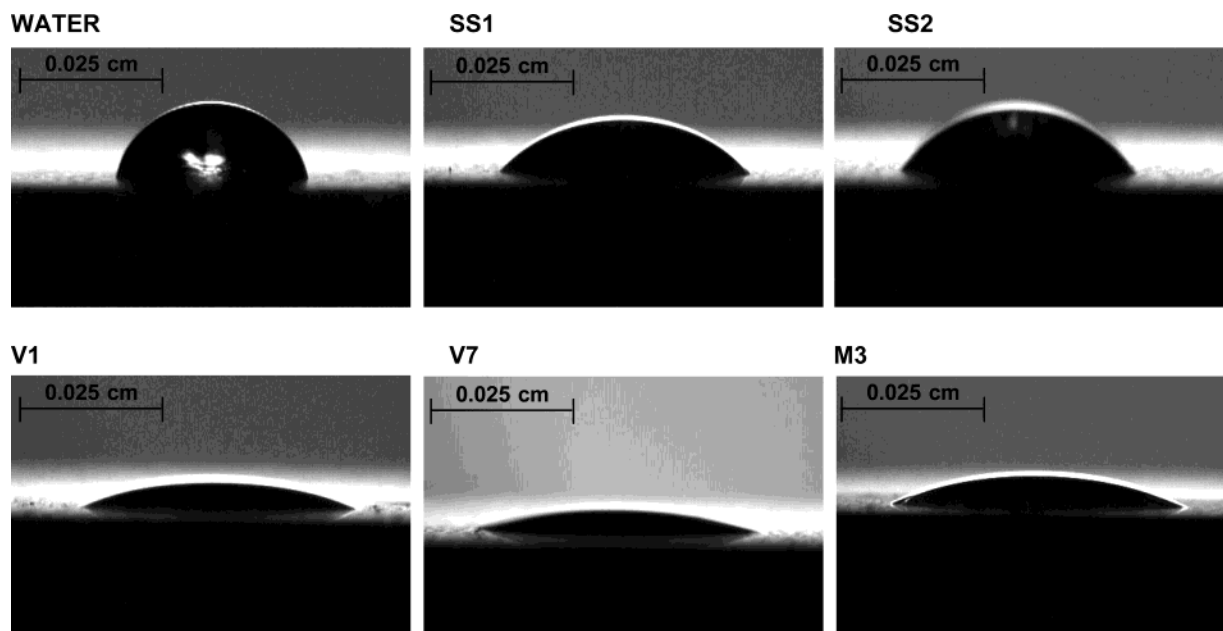
FIGURE 8. Images of deionized water, SS1, SS2, V1, V7, and M3 droplets on 1018 cold rolled steel.
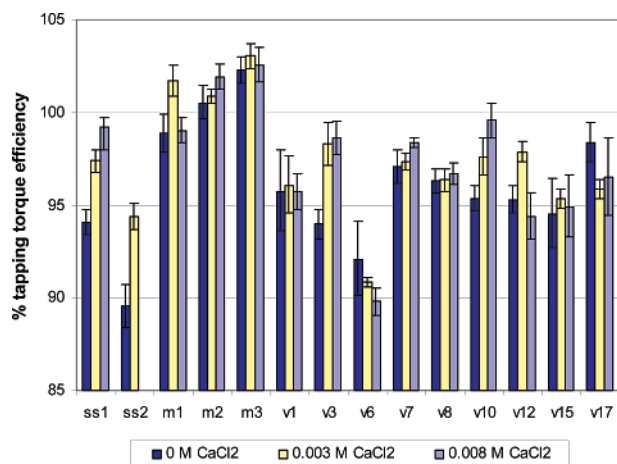

FIGURE 9. Tapping torque efficiency for SS1, SS2, and representative mineral oil- and vegetable oil-based formulations at 0, 0.003, and 0.008 M calcium chloride. Tapping torque data was not reported for SS2 at 0.008 M calcium chloride due to oil–water emulsion separation. Error bars represent 95% confidence intervals.

Environmental Relevance

This research has resulted in the development of novel mineral oil and vegetable oil MWFs that exhibit competitive performance and improved stability under hard water conditions relative to commercially available MWFs. Consistent with the Principles of Green Engineering (7), these MWF formulations offer the likelihood of extended lifetime under hard water conditions while utilizing more inherently benign and renewable components. Experience has shown that MWF lifetime extension reduces environmental and economic impacts related to MWF production and disposal. The newly developed formulations also utilize fewer components than traditional MWFs and eliminate the need for EDTA, further contributing to a reduction in the overall life cycle cost and environmental impacts of MWFs. Consequently, the research described herein provides an example of environmental and economic "win–win", derived from a fresh perspective on MWF design inspired by green engineering.

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