ISTC Reports
Illinois Sustainable Technology Center

Transiently Stable Emulsions for Metalworking Fluids

Peter Bittorf
Shiv G. Kapoor
Richard E. DeVor
Department of Mechanical Science
and Engineering
University of Illinois at Urbana-Champaign

RR-119
December 2011
www.istc.illinois.edu

RR-119

Transiently Stable Emulsions for Metalworking Fluids

Peter Bittorf, Shiv G. Kapoor, and Richard E. DeVor
Department of Mechanical Science and Engineering
University of Illinois at Urbana-Champaign

December 2011

Submitted to the
Illinois Sustainable Technology Center
Prairie Research Institute
University of Illinois at Urbana-Champaign
www.istc.illinois.edu

Printed by the Authority of the State of Illinois
Patrick J. Quinn, Governor

Acknowledgements

The authors would like to thank the Illinois Sustainable Technology Center, a division of the Prairie Research Institute at the University of Illinois at Urbana-Champaign, for their support of the project (Grant No. HWR05191). In addition, the authors would like to thank all of the gracious and helpful staff at the Illinois Sustainable Technology Center for their assistance with data acquisition and analysis. In particular, the authors would like to thank Dr. Nandakishore Rajagopalan for his guidance and support during the project.

Table of Contents

Page

List of Tables

Table Page

List of Figures

Abstract

Modern high speed machining would not be possible without the use of metalworking fluids (MWFs). MWFs perform a number of useful functions like cooling and lubrication. They also assist with metal chip evacuation and short-term corrosion protection. It is estimated that 90 million U.S. gallons of water-soluble MWF concentrate are manufactured annually in the U.S. alone to meet the above needs. MWFs become process effluents when the accumulation of contaminants such as extraneous oil, particulate debris from machining operations, and bacteria negatively impact functionality. One to two billion U.S. gallons of oily wastewater result annually from the use of MWFs. Reducing this environmental footprint has become an important objective for both manufacturers and end-users of MWFs.

Oil-containing MWFs are conventionally formulated to be highly stable emulsions. These emulsions are difficult to maintain, recycle, and treat (Byers, 1994). Preliminary work indicated that transiently stable emulsions can provide comparable lubrication, while also potentially being easier to maintain and recycle. They also offer fewer problems for waste treatment than their stable counterparts. This report focuses on a rational approach to designing such transiently stable emulsions by elucidating the important factors affecting lubrication, cooling, and phase separation.

Chapter 1

Introduction

1.1 Background and Motivation

Modern high-speed machining would not be possible without the use of metalworking fluids (MWFs). MWFs perform a number of useful functions including cooling, lubrication, chip evacuation, and short-term corrosion protection (Byers, 1994). MWFs become process effluents when the accumulation of contaminants such as extraneous oil, particulate debris from machining operations, and bacteria negatively impact functionality (Marano and Carudner, 1991; Abanto et al., 1994; Eppert, 2002; Skold and Tunius, 1994; Khudobin and Polyanskov, 1982; Rinkus et al., 1997). Reducing this environmental footprint has become an important objective for both manufacturers and end-users of MWFs. To this end, microfiltration has proven to be effective in selectively separating semi-synthetic MWFs from contaminants. However, emulsion stability, which is perceived to be a crucial element for MWF performance, gives rise to unintended consequences such as difficulty in water treatment, excessive organic loading, and reliance on biocides, all of which are detrimental to microfiltration.

Recent developments in microfiltration technology have successfully demonstrated the selective separation of semi-synthetic MWFs from contaminants such as bacteria and tramp oil (Rajagopalan et al., 2004). However, MWFs that contain high concentrations of oil often cannot be effectively treated by microfiltration methods because such filters will remove the desired oil component with the other entrained, undesirable components. It has also been shown that the presence of specialty additives such as lubricants, defoamers, and biocides in MWF formulations can significantly reduce the productivity of the membrane filtration process (Skerlos et al., 2000a; Mahdi and Skold, 1990; Misra and Skold, 1999). Furthermore, the abundance of surface-active agents (surfactants), which aid in emulsion stability in commercial formulations, increases the potential for membrane-solute interaction. In short, the potential for membrane fouling and the filtration difficulties that arise with stable MWFs are causes for concern.

Recently, it has been determined that the use of transiently stable emulsions in MWFs show promise in terms of both functional requirements, such as cooling and lubrication, and microfiltration compatibility (Srijaroonrat et al., 1999). Preliminary work has indicated that transiently stable emulsions can provide comparable functionality to industrial MWFs while offering fewer waste treatment problems because of additive reductions (Zimmerman et al., 2004). However, in developing formulations to create such fluids it is important to consider the critical parameters of the oil-water emulsion that have a bearing on the cooling and lubrication properties of the fluid, the effect of the oil phase chemistry on lubrication, and the factors that affect the separation properties of the oil-water emulsion and their behavior over time.

In general, the primary properties of the oil-water emulsion that could have a bearing on the lubrication and cooling properties of a MWF are the proportions of oil and water, the particle size of the emulsion, and physical properties such as viscosity and surface tension. The proportion of oil and water would be expected to impact the lubrication and cooling properties because it affects properties such as viscosity, thermal conductivity, and specific heat. The particle size of the transient emulsion should also be expected to play a role because smaller particles are postulated to effectively lubricate smaller interstitial gaps. However, the need for a very small particle size (less than 1 micron diameter) would require a high input of mechanical energy and an increased need for cooling. The surface tension of the mixture may also play a role in promoting wetting of the tool and facilitating the capillary movement of the emulsion mixture.

If transiently stable emulsion formulations are to gain favor, it will be important to evaluate their performance for the three main lubrication regimes that are commonly used in MWFs: hydrodynamic lubrication; extreme pressure (EP) lubrication; and boundary lubrication. It is clear that the chemical nature of these regimes should have a bearing on the functionality of the fluid. Prior experimental evidence indicates that EP additives have good lubrication properties (Byers, 1994). However, napthenic oil by itself showed very little lubrication. It is well known that EP additives form chemically reactive films that aid in lubrication while napthenic oils perform lubrication by forming load-bearing films (Byers, 1994). From the experiments performed, it would appear that the napthenics could not form sufficient load-bearing films (Byers, 1994). This may be related to other physical phenomena, such as capillary movement and wetting. It may also indicate that lubrication in the hydrodynamic range is not important in machining. However, because commercial semi-synthetic MWFs with napthenics do provide useful lubrication even in the absence of EP additives, it may also indicate the importance of boundary lubrication due to polar oil additives such as fatty acids that are also present in such formulations. At this time there is very limited knowledge available on the concept of transiently stable mixtures for MWFs and the impact of their properties on functionality.

1.2 Research Objectives, Scope, and Tasks

1.2.1 Research Objectives and Scope

The objective of this research was to develop a rational approach to designing transiently stable emulsions by elucidating the important factors affecting lubrication, cooling, and phase separation. To accomplish this, the research had two specific sub-objectives:

1. To understand the lubrication and cooling properties of constituents of transiently stable two-phase mixtures as MWFs

2. To understand the separation kinetics and phase composition of the two-phase mixtures

Through experimental evaluation, this project characterized lubricating and cooling functionality using the metrics of drilling forces (namely torque and thrust) and drill temperature, respectively. The drilling forces and temperature used to characterize lubrication and cooling functionality of the transiently stable two-phase mixtures were investigated using the drilling test methodology developed by Greeley et al. (Greely et al., 2003). These metrics and procedures have been found to adequately characterize MWF lubricating and cooling functionalities (Greely et al., 2003). The workpiece material used in all testing was 1018 steel, which was chosen because of its good machinability and its common use in industry.

The effect of the water phase surface tension was evaluated using mixtures of water and chemicals such as glycol ethers. The effect of viscosity on lubrication was determined in separate experiments by adding block copolymer surfactants. Deionized (DI) water was used as the control.

Lubrication by viscous effects assumes a hydrodynamic lubrication regime. However, this may not be the case, with boundary and EP lubrication possibly having a greater role to play in machining operations. These effects were explored by incorporating polar oils, such as fatty acids having dipole moments, or EP additives, such as chlorinated paraffins, active sulfur or phosphorous compounds.

Separation kinetics and phase composition investigations were restricted to particle size distribution measurements and centrifugation. The addition of heat was the only variable used to enhance separation results.

1.2.2 Research Tasks

The objectives outlined above were met by completing the following specific tasks:

1. **Investigate the effect of the water phase surface tension and viscosity on the MWF cooling functionality.**

The effect of the water phase surface tension was evaluated using mixtures of water and ethers (e.g., the Dowanol Series from Dow Chemical). Water and ether mixtures are similar to water in viscosity and specific heat, which allows determination of the contribution of surface tension to cooling. The effect of viscosity on lubrication was determined in separate experiments by adding UCon series non-ionic polyalklene glycols such as 50-HB-660. The glycol is completely soluble in water and in Dowanol ethers, making it possible to produce mixtures with widely varying viscosities for testing purposes. DI water was the control fluid.

2. **Investigate the effect of an extreme pressure additive on MWF lubrication functionality.**

The oil phase, comprised of an EP additive, provided the lubrication. The viscosity of the water phase was not adjusted. The variables of interest are the surface tension of the water phase, the particle size of the emulsion, and the proportion of oil. The effect of these factors and their importance were explored by a design of experiment

(DOE) approach. The particle size of the emulsion was varied by the manufacturing method, blending for varying lengths of time with a laboratory grade blender. Based on the results of the experiments, the most important factors and their interactions were identified to guide further experimentation.

3. **Investigate the effect of a boundary lubricant on MWF lubrication functionality.**

The same DOE approach that was used for the EP additive was employed, but the lubrication was provided by the oil phase comprised of a boundary lubricant.

4. **Formulation and investigation of the custom two-phase metalworking fluids.**

Based on information collected from the DOEs, mixtures of oil-water with desired metalworking functionality were formulated. The pH was adjusted to 9 to retard corrosion and bacterial growth. In real systems, use of organic corrosion inhibitors is anticipated but avoided here to minimize potential interaction effects.

5. **Investigate the MWF emulsion stability characteristics.**

The ability of the oil-water mixture to separate into two relatively pure phases is of interest. Factors affecting such separation include particle size, phase density and Derjaguin-Landau-Verwey-Overbeek (DLVO) forces. Moreover, with continued use, the oil phase could undergo chemical changes, such as oxidation, that could change the stability characteristics of the emulsion. Separation kinetics were determined by analyzing the quantity of oil phase separating out over time. The stability of the oil-water mixture is expected to be a function of the interfacial tension, particle size, and DLVO forces stabilizing the mixture. The effect of centrifugation and coalescing media on accelerating phase separation was investigated.

6. **Validate the customized formulation versus an industrial MWF.**

A representative oil-water mixture formulated and evaluated in the previous phases was tested for a limited period of time under normal machining conditions. The testing focused on the cooling and lubrication functionality of the transiently stable two-phase mixture. Purification, if necessary, was accomplished primarily by settling, separation of the water phase, and replacing with fresh water. A commercial MWF and DI water were used for control studies.

1.3 Report Outline

Chapter 2 of this report reviews relevant literature on metalworking fluid (MWF) formulation techniques, microfiltration, lubrication regimes, emulsion stability, and performance evaluation methods. Specifically, we detail: investigations into MWF additives and their effect on microfiltration fouling; the influence of emulsion stability on microfiltration functionality and fluid performance; and the mechanisms used for lubricity by different lubrication regimes. Finally, we evaluated the MWF tapping torque evaluation and a drilling-based methodology.

Chapter 3 contains an in depth account of the effect of water phase surface tension and viscosity (provided by hydrodynamic lubrication) on MWF functionality. The link between these fluid properties and the functionality of the MWF was examined in terms of cutting forces and machining temperature. The testing methodology that was carried out on an instrumented drilling test-bed to evaluate the effect of the fluid properties on cutting temperatures and forces is detailed. Finally, the findings that are described confirm that surface tension and viscosity of cutting fluids play important roles in cooling and lubrication of the drilling process.

Chapter 4 examines the lubrication functionality of the EP and boundary regimes. The oil phase was introduced to provide additional viscosity and lubrication to the solution, while the water phase was adjusted to optimal surface tension, as found from testing in Chapter 3. Also, the effects of surface tension, particle size, and proportion of oil in the mixture on the MWF functionality were evaluated by a design of experiment (DOE) approach. Based on the DOE results, the most important factors that influence drilling temperatures and forces were identified, which in turn guided further experimentation and formulation.

Chapter 5 explores the formulation and investigation of the custom two-phase MWF, the separation kinetics and phase composition of the two-phase mixtures, and the validation studies. Based on the three lubrication regime studies, the customized MWF formulation development is discussed. This formulation was evaluated on whether the transiently stable mixture was able to separate to provide relatively clean water and oil phases. Machining tests were conducted to assess the cooling and lubrication functionality of the transiently stable custom formulations compared with industrial fluids. Finally, based on the initial machining tests, reformulations were developed and evaluated in identical machining tests. The results of the machining tests are discussed in detail.

Chapter 6 contains summaries and conclusions regarding the research presented and recommendations for future work.

Chapter 2

Literature Review

This chapter reviews relevant literature on metalworking fluid (MWF) formulation techniques, microfiltration, lubrication regimes, emulsion stability, and performance evaluation methods. Specifically, this chapter details: investigations into MWF additives and their effect on microfiltration fouling; the influence of emulsion stability on microfiltration functionality and fluid performance; and the mechanisms used for lubricity by different lubrication regimes. Finally, we evaluated the MWF tapping torque evaluation and a drilling-based methodology.

2.1 Metalworking Fluid Composition

2.1.1 Metalworking Fluid Classification Overview

MWF chemistry has evolved from simple oils to refined water-based technology. This evolution is shown in Figure 2.1 (Byers, 1994). There are four basic classifications of MWFs: insoluble oils, soluble MWFs, synthetic MWFs, and semi-synthetic MWFs (Gauthier, 2003). Depending on the specifics of the application, any one of the four can be used successfully.

Water-based MWFs can be divided into three basic categories: soluble oils, semi-synthetics, and synthetics (Byers, 1994). In general, these are differentiated by the amount of mineral oil present in the concentrate. Soluble oils typically have 60 – 90% mineral oil in the concentrate with the balance made up mostly of emulsifiers to keep the oil stable in the water phase. Semi-synthetic fluids are similar, except they have much lower oil content than soluble oils, i.e., in the range of 2 – 30%. The concentrates are normally diluted with water before use. Dilutions range from 5:1 to 10:1. Synthetic fluids contain no mineral oil. Semi-synthetic and soluble oils represent about 80% of all water soluble MWFs in the U.S. market. Therefore, they are the primary focus of this research.

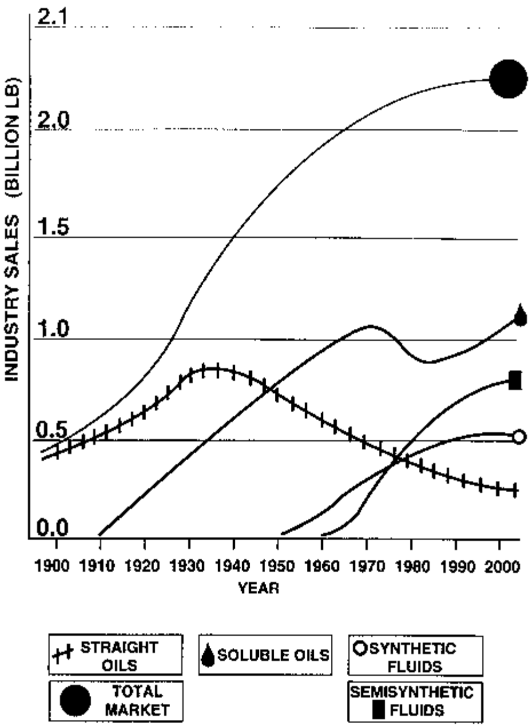


Figure 2.1. Metalworking Fluid Evolutionary Product Life Cycle (Byers, 1994).

Regardless of the MWF type, the single most important maintenance item that must be routinely measured is MWF concentration (Benes, 2006). Most MWFs are designed to be mixed with water either by adding the MWF to an existing solution, by premixing or, by mixing with a proportioner. Automatic MWF proportioners help ensure uniform concentrations. Whichever method is used, solutions can be kept at optimum levels and costs can be tracked if MWF and water additions are meticulously recorded.

Straight Oils. These formulations contain no water and are comprised of petroleum or vegetable oils. Frequently referred to as cutting oils, straight oils are used as lubricants. They improve the finish on the cut surface and prevent rusting. The petroleum oils used in MWFs are usually light solvents, neutral oils, or heavy bright and refined stocks. Animal, marine, or vegetable oils may also be used singly or in combination with mineral oils to increase wetting action and lubricity. The oil can also be compounded with various polar and/or chemically active additives. Straight oils provide hydrodynamic lubrication. When compounded with lubricant additives, they are useful for severe cutting operations, for difficult to machine metals, and, overall, require fewer additives than the soluble types (Byers, 1994; Gauthier, 2003).

Paraffinic oils, which are often used in straight oils, offer better oxidative stability and less smoke generation during cutting than naphthenic oils (Byers, 1994). However, most compounded oils contain naphthenic oils because the lubricant additives are more soluble and compatible in naphthenic oils (Silliman, 1992).

Soluble or Emulsifiable Oils. With the changeover to carbide tooling and increased machine speeds, water-diluted MWFs were developed. These emulsions and water-soluble oils are designed to cool and lubricate. The fluids reduce abrasive wear of the tool at high temperatures and prevent thermal distortion caused by residual heat. The highly-refined mineral oils of soluble MWFs are blended from higher viscosity oil bases than are insoluble oils. Soluble MWFs concentrates are diluted with water at different ratios before use and contain a surface-active emulsifying agent (surfactant) to maintain the oil-water mix in an emulsified oil and water phase. The product concentrate, which is oil fortified with emulsifiers and specialty additives, is diluted at the user's site with water to form emulsions. There are two types of emulsions: oil-in-water (o/w) and water-in-oil (w/o or invert) (Canter, 2005). In the former, oil droplets are dispersed in a continuous water phase, see Figure 2.2 (Byers, 1994; Gauthier, 2003). The latter represents the reverse case in which water droplets are present in a continuous oil phase.

Synthetic MWFs. Synthetic MWFs do not contain oil. The simplest synthetics are composed of organic and inorganic salts dissolved in water. Also functioning as coolants and lubricants, synthetic MWFs eliminate smoke generation, reduce misting, provide detergent action, and reduce oxidation. Consequently, the simple synthetics offer rust protection and good heat removal but usually have very low lubricating ability. Synthetics are stable and can be supplemented with biocides to discourage the growth of microorganisms. They also provide effective cooling capacity at high machining speeds and feedrates (Byers, 1994; Gauthier, 2003).

Semi-Synthetic MWFs. This class of MWFs contains small amounts of oil (5 – 30%) in the concentrate and may be formulated with fatty acids, sulfur, chlorine, and phosphorous to provide lubrication for higher speed and feedrate operations. The same extreme-pressure (EP) additives that are used for insoluble oils may also be added to

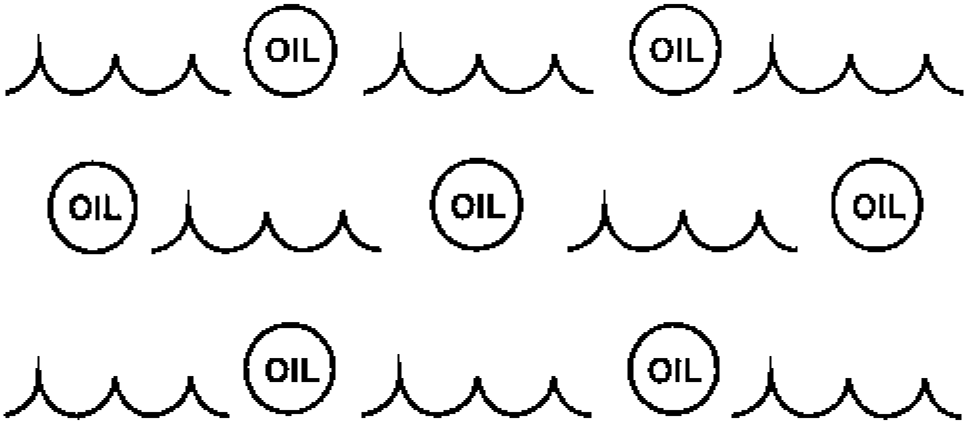


Figure 2.2. Oil-in-water Emulsion (Byers, 1994).

water-soluble oils. Coupling agents are used to maintain emulsification. Antifoaming agents, dyes, perfumes, and water softeners may also be added. Biocides may be added to reduce the growth of bacteria and fungi in water-based fluids (Byers, 1994; Gauthier, 2003). The presence of water in the soluble fluids can cause machine tools and parts to corrode. Consequently, amines and certain oils may be added to inhibit corrosion (Gauthier, 2003).

2.1.2 MWF Additive Types

The chemical additives used in MWFs serve various functions. These include emulsification, corrosion inhibition, lubrication, microbial control, pH buffering, coupling, defoaming, dispersing, and wetting (Byers, 1994).

In general, these additives are used to make a fluid stable, low-foaming, and waste-treatable. Many properties of additives are mutually exclusive. Typically, if a fluid has excellent biological and hard-water stability, it may be difficult to waste treat (Byers, 1994). Or if it provides excellent lubricity, it may be difficult to clean.

Surface active agents (Surfactants). In industrial MWFs, surface active agents, or surfactants, such as emulsifiers, soaps, and detergents are used to reduce the surface tension of the fluid, thereby promoting good coverage of the tool and workpiece for cooling (Byers, 1994). They are also widely used to stabilize the oil and water components present in emulsifiable formulations (Canter, 2005). They contain both a hydrophilic group that has affinity for water and readily goes in suspension in water, and a lipophilic group that is soluble in oil and oil-soluble components. Emulsions by nature contain both aqueous and nonaqueous species existing in a stable environment. Surfactants operate at the boundary between oil- and water-soluble components.

Since surfactants are critical components in a MWF, the formulator needs to be as precise as possible in selecting the proper surfactants to prepare a stable product (Canter, 2005). This selection of the surfactant is achieved today by using the hydrophile/lipophile (affinity for water/affinity for oil) balance (HLB number). The key to the process is that each nonionic surfactant, or blend of surfactants, has a specific HLB value. Likewise each component, or blend of components, has a specific HLB requirement. Matching the HLB requirement of the system with the HLB value of the surfactant(s) yields optimum performance/cost relationships. In other words, the HLB number attempts to match the oil-/water-soluble needs of the MWF system with the surfactants that will provide this optimum relationship.

HLB values can range from 2 to 18 depending upon the composition of the nonionic surfactant (Canter, 2005). These values can be determined by dividing the weight percent of the hydrophilic component by 5. As the HLB value increases, the surfactant becomes more hydrophilic and less lipophilic. For example, preparation of a water-in-oil emulsion will require surfactants with HLB values between 4 and 6. In contrast, preparing an oil-in-water emulsion requires surfactants exhibiting HLB values between 8 and 14.

Hetsroni et al. (2004) evaluated whether surfactants enhance the boiling of water. Their experimental results demonstrated that the heat transfer of the boiling process can be enhanced considerably by the addition of a small amount of surfactant. The heat transfer was shown to increase continuously as concentrations are increased. Wen and Wang (2002) also provide data that illustrate that under nucleate pool boiling conditions, surfactants do enhance heat flux. Lower surface tension allows for formation of smaller bubbles that are generated at greater frequency, leading to higher heat flux. It follows that in machining, a MWF with enhanced heat transfer properties would provide better cooling functionality by transferring more heat from the cutting zone.

Lubricants. Hunz (1984) reviewed lubricants within water-based MWFs. He points out that lubricity agents are used along or combined with EP additives to prevent tool-workpiece welding. He also states that lubricity agents reduce the frictional heat generated. Inversely soluble esters are less soluble in hot water than in cold. Thus, as the coolant containing them is circulated, they remain in solution. Then, when the coolant comes into contact with the cutting zone, the heat generated by the action of the tool and the sliding chip causes the ester to come out of solution to provide lubrication. Once the temperature of the coolant drops, the lubricant goes back into solution. Hunz proposed that inversely soluble additives will provide a hydrodynamic layer of lubrication.

In operations such as drawing and forming where a tougher hydrodynamic lubricant barrier film is necessary, oils with high viscosity are used (Byers, 1994). In chip removal operations such as drilling, highly viscous oils will not clear chips well and can act as an insulator, reducing the cooling properties of the fluid. Thus, a MWF should have a viscosity that is low enough to allow good chip removal and not reduce cooling functionality, but it should be high enough to provide a friction-reducing hydrodynamic layer.

The thickness of adsorbed molecular layers is the most critical factor in studying thin film lubrication and is a key feature that distinguishes thin from thick film lubrication. Quingwen et al. (2002) present a method that enables the adsorbed layer thickness to be calculated. This is based on adsorption theory and expressed in terms of molecular interaction energies. A continuous cross-gap viscosity model incorporating the layer thickness is introduced and used to calculate the load capacity and frictional characteristics of a simple bearing operating in the thin film regime. It was found that the importance of the adsorbent layer is mainly due to its influence on the liquid viscosity. Adsorbent action is important for thin film analysis and will be of guiding significance for thin film lubrication.

Yan and Kuroda (1997) investigated the viscosity coefficients of emulsions and two sets of formulas are suggested for their determination. The formulas are suitable for two different states of emulsion, viz., in the thick film zone and in the thin film zone. On this basis, they discuss the variation of the oil concentration along the lubrication film, as well as the reason why the hydrodynamic lubrication film thickness of emulsions is of the same order as that of straight oils. Yan and Kuroda (1997) predict that the concentration process of the oil phase of oil-in-water emulsions also occurs in the thick film zone, although the size of an oil droplet in the emulsion is smaller than the film thickness there.

In the thin film zone, for oil-in-water or water-in-oil emulsions, the concentration process of the oil phase will occur. Because the general hydrodynamic film thickness of an emulsion is smaller than the droplet size, the increase in oil concentration makes it the same order as straight oils. Therefore, for either oil-in-water emulsions or water-in-oil emulsions, the oil concentration will increase in the direction of movement.

Vegetable Oils. Another MWF-chemistry innovation is the substitution of vegetable oils for mineral oils in formulations that use soluble-oils (Benes, 2006). While vegetable oils are rapidly biodegradable in waste-treatment systems, they simultaneously present bacteria with a prime food source and promote faster bacterial growth in sumps. Although these soluble oils provide more lubrication than mineral oils, they do not improve the difficulties associated with the absorption and separation of tramp oils. Vegetable oils also are harder to emulsify and their emulsions tend to exhibit poor stability. As with mineral oils, they become destabilized through heat-induced oxidation, and they can yield oily residues and mists.

2.2 Microfiltration

Traditional practice has been to dispose of used MWFs as the contaminant levels from sources such as lubricating oils, hydraulic oils, rust inhibitors, floor cleaners, and heat-treat solutions increase. However, because they are stable as oil-water mixtures, MWFs create both monetary and environmental problems for waste treatment and disposal. It is estimated that 90 million U.S. gallons of water-soluble MWF concentrate are manufactured annually in the U.S. alone (van Antwerpen, 2000). One to two billion U.S. gallons of oily wastewater results each year from the use of MWFs (Cheryan and Rajagopalan, 1998).

The high share of the costs for cooling and lubrication technology reaches nearly 20% of the total manufacturing costs (Brockhoff and Walter, 1998). Comparing the costs for MWFs and cutting tools, which make up only 7.5% of the total costs, it is difficult to understand why all innovations and activities for cost improvement in the last couple of decades were focused on cutting tools. MWF consumption can be reduced by improved recycling methods, which is illustrated by recent developments in microfiltration technologies. These processes selectively separate MWF from contaminants such as bacteria and tramp oil.

2.2.1 Microfiltration Overview

A synthetic membrane, most often polymeric, is used as a selective barrier in microfiltration processes. Certain feed stream components are permitted passage by the membrane pores into a permeate stream, while other, usually larger feed components, are retained by the membrane (Van der Bruggen et al., 2003). These retained species accumulate in the retentate stream. Pressure-driven membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the water through the membrane (Van der Bruggen et al., 2003). Particles and dissolved components are partially retained based on properties such as size, shape, and charge.

In industrial full-scale installations, the ratio between permeate stream and the feed stream ranges from 50 – 90%, but is typically around 80%.

Pressure-driven membrane processes can be classified by several criteria: the characteristics of the membrane (pore size); size and charge of the retained particles or molecules; and pressure exerted on the membrane. This classification distinguishes microfiltration from ultrafiltration, nanofiltration, and reverse osmosis (see Figure 2.3). Characteristics of all these processes are summarized in Table 2.1. Microfiltration membranes have the largest pores (ranging from 0.1 – 10 µm) and the highest permeability, so that a sufficient water flux is obtained at a low pressure. The smallest pore sizes correspond to the size of suspended solids, colloids, and bacteria. Components larger than the pore size are removed by a sieving mechanism. Microfiltration is also known to be an efficient process for removing particles that may cause problems in further treatment steps (Van der Bruggen et al., 2003).

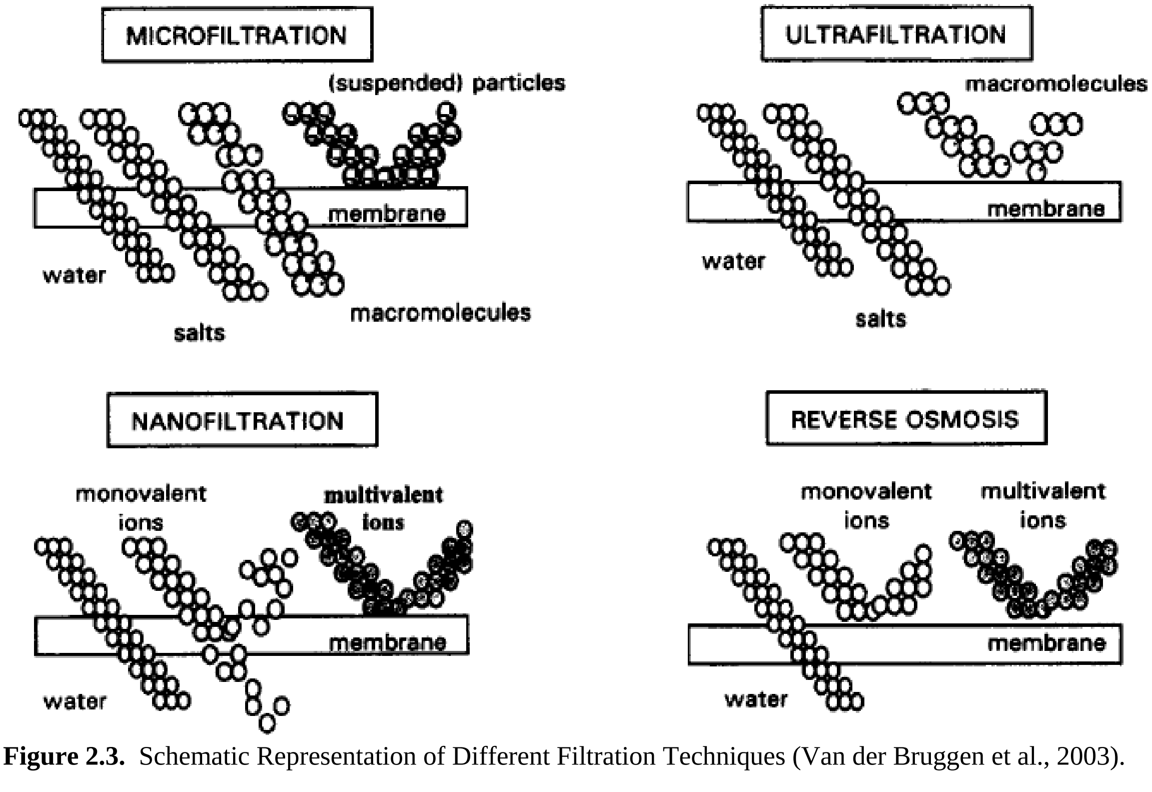
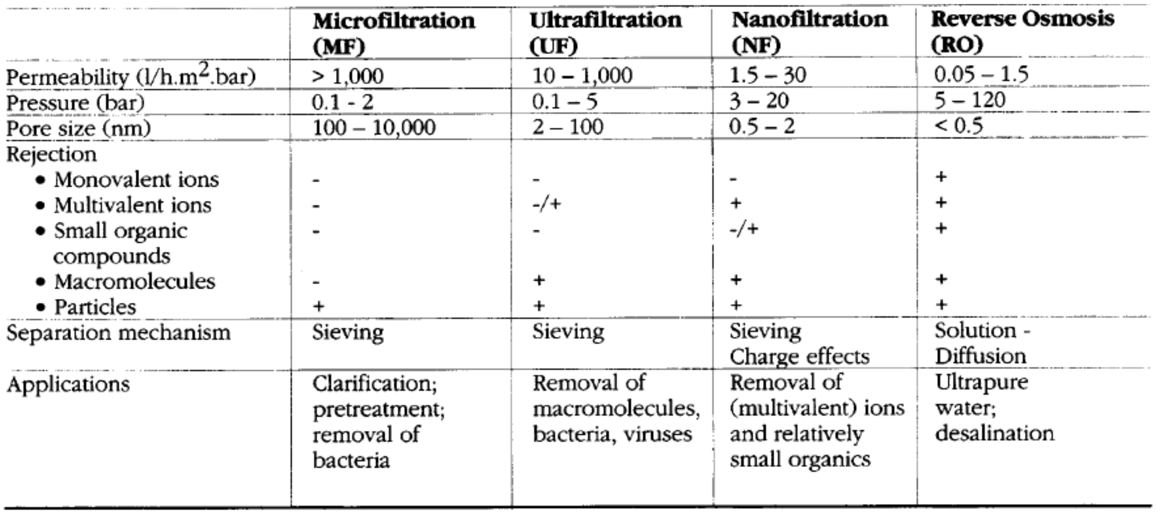


Figure 2.3. Schematic Representation of Different Filtration Techniques (Van der Bruggen et al., 2003).

Table 2.1. Overview of Different Filtration Techniques (Van der Bruggen et al., 2003).



	Microfiltration (MF)	**Ultrafiltration (UF)**	**Nanofiltration (NF)**	**Reverse Osmosis (RO)**
Permeability (l/h.m^2.bar)	> 1,000	10 – 1,000	1.5 – 30	0.05 – 1.5
Pressure (bar)	0.1 - 2	0.1 – 5	3 – 20	5 – 120
Pore size (nm)	100 – 10,000	2 – 100	0.5 – 2	< 0.5
Rejection				
• Monovalent ions	-	-	-	+
• Multivalent ions	-	-/+	+	+
• Small organic compounds	-	-	-/+	+
• Macromolecules	-	+	+	+
• Particles	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving Charge effects	Solution - Diffusion
Applications	Clarification; pretreatment; removal of bacteria	Removal of macromolecules, bacteria, viruses	Removal of (multivalent) ions and relatively small organics	Ultrapure water; desalination

2.2.2 Microfiltration Functionality Studies

Microfiltration has the potential to reduce health risks and extend MWF life in the machine tool industry. A study was conducted to assess the productivity of ceramic membrane filters during filtration of synthetic MWFs and examine the contribution of MWF chemical ingredients to membrane filter productivity decline (Skerlos et al., 2000a). It was found that the majority of the chemistry comprising typical synthetic MWFs has negligible impact on microfiltration productivity. However, specialty additives such as lubricants, defoamers, and biocides can significantly reduce microfiltration productivity. Results showed that slight variations in formulation can dominate the productivity of the process. Specialty additives can also impart residual effects on the membrane that adversely impact productivity in subsequent applications of the ceramic membrane. Due to the sensitivity of membrane filtration productivity to low concentration specialty additives, specialty additives require particular attention with respect to their chemistry and use concentration when optimizing MWF formulations with respect to membrane filtration recycling.

The predominant mechanism of flux decline during microfiltration of a synthetic MWF was revealed from an analysis of flux data obtained during another experimental investigation (Skerlos et al., 2000b). The decline appears to be adsorptive interactions occurring at the membrane surface. Field Emission Environmental Scanning Electron Microscopy (FE-ESEM) images of aluminum oxide membranes after MWF microfiltration illustrated that adsorption leads to reduction in pore diameter that serves to reduce flux. The bulk of the pore constriction and flux decline caused by the synthetic MWF was accounted for by a diblock copolymer surfactant used as an inversely soluble hydrodynamic lubricity additive. FE-ESEM images also revealed that the mechanism of flux decline from a defoamer varies depending on the presence of lubricant additive in solution. In the absence of lubricant additive, the defoamer forms a cake layer at the membrane surface, as shown in Figure 2.4. In the presence of the lubricant additive, the defoamer adsorbs to the surface of the membrane with the lubricant additive to constrict pores. In contrast to the lubricant additive and defoamer, base fluid flux decline observed after specialty additive exposure cannot be accounted for by adsorption leading to pore constriction. Figure 2.5 shows examples of physical obstruction to permeation.

A different investigation examined chemical characteristics of MWFs that can lead to flux decline during microfiltration using aluminum oxide membranes (Skerlos et al., 2001). This study examined the family of polyoxyalkylene diblock copolymers composed of ethylene oxide and propylene oxide. These copolymers are commonly used as lubricant additives in MWFs and serve as a model for beginning to understand the relationship between MWF formulation and microfiltration flux. It was found that increasing the hydrophobic content of the copolymers can lead to reduced flux.

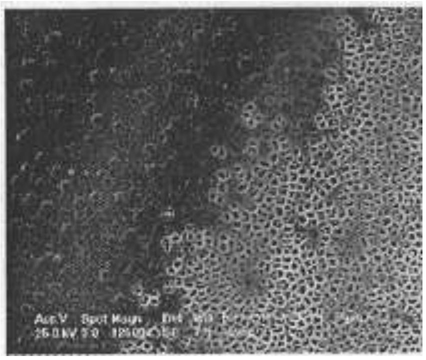


Figure 2.4. Transition Region between Cake Layer formed by a 0.025 percent Dispersion of Defoamer in Water and Portion of Membrane not exposed to Defoamer (Skerlos et al., 2000b).

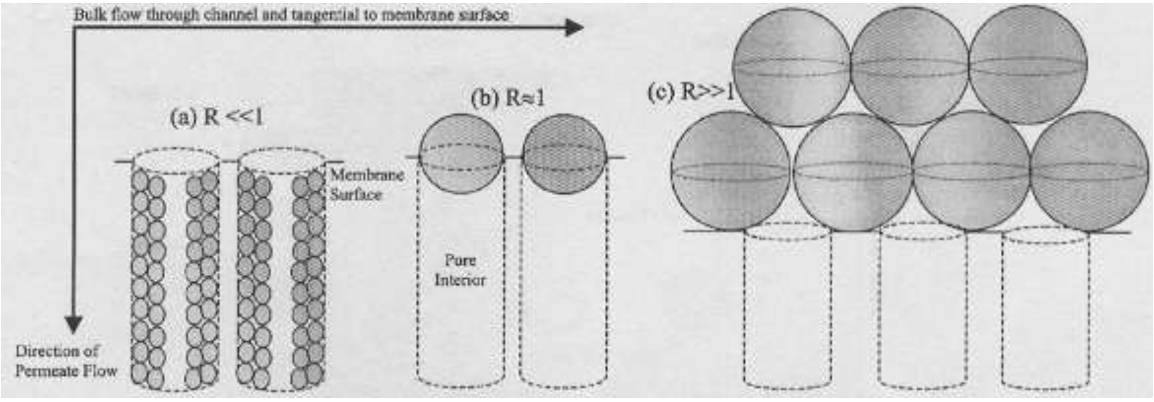


Figure 2.5. Examples of (a) Pore Constriction Due to Adsorption, (b) Pore Blocking due to Physical Lodging of Particulate, and (c) Cake Formation due to Size-exclusion (Skerlos et al., 2000b).

Anionic modification and increasing molecular weight of the copolymers can also lead to reduced flux. Insufficient cleaning of anionic copolymers from the membrane leads to pH-dependent flux of DI water during subsequent filtration. The pH-dependence of flux arises from swelling caused by electrostatic repulsions between the aluminum oxide surface and anionic copolymers that remain adsorbed to the surface of the membrane. This swelling serves to resist permeate flow above the isoelectric point of aluminum oxide.

During the microfiltration of uncontaminated synthetic MWFs using aluminum oxide membranes, the interaction of relatively low concentration specialty additives with the membrane surface has a significant effect on the overall productivity (Skerlos, 2001). In the case of polyglycol copolymers used as hydrodynamic lubricity additives, adsorption leading to pore-constriction and increased resistance to flow is the dominant mode of flux-decline. The concentration of these additives has a significant effect on the maximum achievable filtration rate of the process.

2.3 MWF Lubrication Regimes

There are three main lubrication regimes that are commonly used in MWFs: hydrodynamic lubrication; extreme-pressure lubrication; and boundary lubrication. Hydrodynamic lubrication is a system of lubrication in which the shape and relative motion of the sliding surfaces cause the formation of a fluid film having sufficient pressure to separate the surface (Byers, 1994). EP lubricants use a compound (usually containing chlorine, sulfur, or phosphorus) that reacts with the surface of the metal or tool to form compounds (chlorides, sulfides, or phosphates) which have low shear strength. Boundary lubrication is a condition in which the friction between two surfaces in relative motion is determined by the properties of the surfaces and by the molecular attraction of the lubricant to the metal surface (Byers, 1994). These three lubrication regimes are generally used concurrently in industrial MWFs to enhance friction reduction.

2.3.1 Hydrodynamic Lubrication

In the hydrodynamic regime of lubrication, also called thick- or full-fluid film, the two surfaces are completely separated from each other by a continuous fluid film (Nachtman and Kalpakjian, 1985). The thickness of the film is about 10 times the magnitude of the surface roughness of the mating surfaces. The fluid film can be developed hydrostatically by entrapping the lubricant or by using the wedge effect, which is achieved by sliding surfaces in the presence of a viscous fluid at the interface. In this type of lubrication, the bulk properties of the lubricant, specifically viscosity, are important. Chemical effects of the lubricant on metal surfaces are not significant.

In hydrodynamic lubrication, the loads are usually light and the speeds are high (Nachtman and Kalpakjian, 1985). The coefficient of friction is very low, generally between 0.001 and 0.02. There is no wear, except due to any foreign matter that may have entered the lubricating system. The film thickness can be reduced by decreasing the viscosity (such as due to a rise in temperature), decreasing the sliding speed, or increasing the load. Accordingly, the surfaces become close to each other and the normal load between the tool or die and the workpiece is supported partly by the fluid film in hydrodynamic pockets in the surface roughness of the interfaces and partly by metal-to-metal contact of the surfaces. This is generally referred to as mixed lubrication and also as quasi-hydrodynamic.

The film thickness of the quasi-hydrodynamic regime is less than three times the surface roughness (Nachtman and Kalpakjian, 1985). The coefficient of friction may be as high as about 0.4. Forces and power consumption may increase substantially, and wear can be significant. The hydrodynamic pockets also serve as reservoirs for supplying lubricant to those regions at the interface that are starved for lubricants. This type of lubrication, unlike pure hydrodynamic lubrication, is more representative of what occurs in metalworking processes.

2.3.2 Extreme-Pressure Lubrication

Extreme-pressure (EP) additives were developed in response to machining conditions where layers must be formed on the metal surfaces resistant to over 500 °C (Madakovic, 1999). Chlorinated paraffins, such as trichloroethane, represent the most frequently used EP additives in MWFs. They provide an extremely low friction coefficient on metal surfaces at temperatures between 250 and 570 °C. However, because of the demands for a reduction in the use of these compounds due to the problems of calcination and to the increasingly high temperatures required, this additive is no longer acceptable (Madakovic, 1999).

Today, different phosphorated compounds or a combination of different compounds are increasing in use as EP additives. As a result, mono/diester phosphoric acids have seen increased use (Madakovic, 1999). The primary advantages of such esters are that they are inversely soluble; form metal phosiphide layers on metal surfaces in boundary lubrication conditions; and melt at 950 °C. These esters are also good corrosion inhibitors. However, obstacles to the wider application of such esters in traditional formulations include unpleasant odor and color and poor stability in concentrate or emulsion form. Figure 2.6 and Table 2.2 summarize all known EP additives for water-soluble MWFs, classified according to activation temperature and temperature range of the lubricating film.

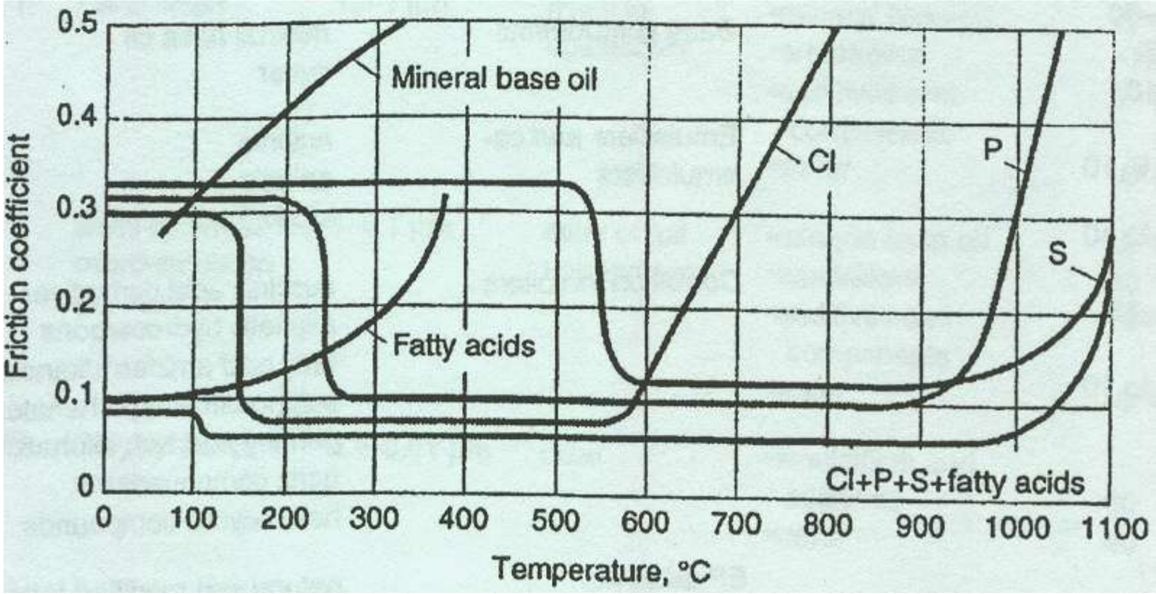


Figure 2.6. Temperature Effect on EP Additive Activity (Madakovic, 1999).

Table 2.2. Classification of EP Additives according to Application Range of Lubricating Film (Madakovic, 1999).

Type of EP additive	**Lubricating film**	**Formation of layer, °C**	**Melting point, °C**
Fatty acids	salts		to 200
Chlorine (i.e., chlorinated paraffins)	FeCl	180	670
Phosphorus (i.e., phosphoric esters)	metal phosphide	280	950
Sulphur (i.e., sulphurised oil)	metal sulphide	520	1100

2.3.3 Boundary Lubrication

In boundary lubrication, a thin layer of lubricant film physically adheres to the surfaces by molecular forces (van der Waals) or by chemical forces (chemisorption) (Nachtman and Kalpakjian, 1985). Boundary films can form rapidly on clean surfaces, although reactivity on some metals, such as titanium and stainless steel, is very low. Lubrication may then be enhanced by the formation of boundary films on tool and die surfaces instead of on the surface of the workpiece.

In hydrodynamic lubrication, the bulk properties of the lubricant are important. By contrast, the chemical aspects of the lubricant and its reactivity with the metal surfaces are more important in boundary lubrication (Nachtman and Kalpakjian, 1985). In this regime, the coefficient of friction usually ranges between 0.1 and 0.4, depending on the strength and thickness of the boundary film. Boundary lubrication is often used in metalworking operations.

Wear rate in boundary lubrication depends on the rate at which films are destroyed by rubbing off or by desorption due to excessive temperatures generated during the metalworking process (Nachtman and Kalpakjian, 1985). If the protective boundary layer is destroyed, friction and wear will be high. Therefore, the adherence and strength of this film is a very important factor in this regime's effectiveness. The role of pressure, speed, and viscosity on film thickness should also be recognized, as shown by the Stribeck Curve in Figure 2.7.

2.4 MWF Emulsion Stability

2.4.1 Definition of Emulsion Stability

In soluble oils, emulsion stability is believed to be the most critical property. The fluid concentrate must be stable without clouding or separating for a minimum of six months storage (Byers, 1994). The emulsifier system must be balanced based on its alkalinity, acidity, and HLB number (Canter, 2005) to ensure an emulsion with no cream or oil forming at the surface of the fluid. The stability of metalworking emulsions is considered a critical characteristic impacting its usefulness as a lubricant and rust inhibitor. Loss of stability usually results in replacement of the fluid, leading to both economic loss and environmental discharge (Deluhery and Rajagopalan, 2005).

A MWF emulsion is comprised of a number of emulsion particles suspended in aqueous media. When made up in deionized (DI) water, these particles scatter light with a characteristic scattering coefficient. Formulated MWF emulsions are typically stable for long periods due to charge repulsion. The charge in most MWF emulsions is due to emulsifiers such as sodium petroleum sulfonate in combination with other anionic stabilizers.

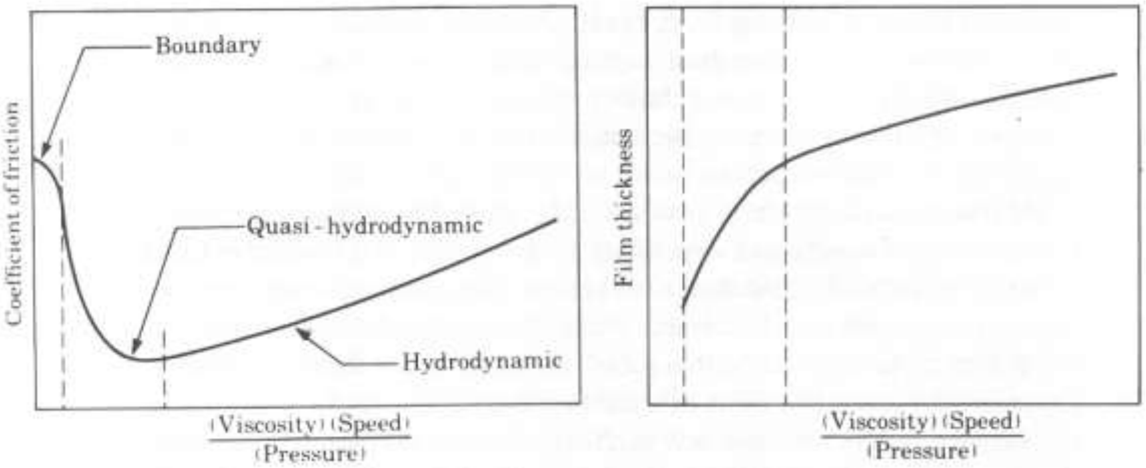


Figure 2.7. Stribeck Curve showing Various Lubrication Regimes as a function of Viscosity of the Lubricant, Sliding Speed, and Interface Pressure (Nachtman and Kalpakjian, 1985).

The Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory describes the force between surfaces interacting through a liquid medium. It combines the effects of van der Waals attraction and the repulsion due to the double-layer of counter-ions. In accordance with the DLVO Theory, when divalent cations such as calcium are introduced, they screen the negative charges present on the emulsion and lower the repulsive barrier which increases the probability of flocculation (Deluhery and Rajagopalan, 2005). In other words, the stability of the emulsion is lowered.

As most oil-in-water emulsions such as MWFs are primarily charge-stabilized, factors that lower the charge of the emulsion particle lead to destabilization of the emulsions. Accumulation of ions (e.g., calcium and magnesium) from sources such as the water used for product dilution has been identified as being responsible for emulsion destabilization [32].

2.4.2 Napthenic Oils and Stability

The properties of naphthenic oils relevant to emulsions of water and oil are well known and documented. That the emulsion's stability is better with naphthenic versus paraffinic oil has been clearly demonstrated (Serra-Holm, 2002). Conventional emulsions – where the concentrate only contains oil and additives – were the subject of the study. That report looked at a special group of MWFs, viz., rust inhibiting agents, and concluded that emulsions of naphthenic oils are considerably more stable than emulsions formed from paraffinic oils.

Semi-synthetic MWFs, which contain higher amounts of emulsifiers and lower amounts of oil than conventional emulsions, contain considerable amounts of water. Such concentrates appear totally clear but are actually a micro-emulsion with very small oil drops, on the order of 0.01 – 0.1 µm in diameter.

A study by Serra-Holm (2002) was conducted to compare both naphthenic- and paraffinic-based concentrates of semi-synthetic fluid to determine on whether semi-synthetic MWFs are affected in the same way as other emulsions by the choice of oil. The formulation used in that study is given in Table 2.3. The aim was to create a micro-emulsion; thus the result should have been a clear and totally transparent fluid. This was the case with the naphthenic oil. However, the paraffinic oil resulted in a milky and coarse emulsion which started to separate immediately and after 48 hours had separated completely into two phases. The emulsion formed from the naphthenic oil was still stable several months after the experiment was completed.

Table 2.3. Naphthenic versus Paraffinic Test Formulation (Serra-Holm, 2002).

Component	**Weight %**
Mineral Oil	23
Erucic Acid	2
Sodium Sulphonate	5
Fatty Acid Tall Oil	3.5
Anionic Emulsifier	1
Nonionic Emulsifier	1.5
Coupling Agent	2.5
Water	38.6
Monoethanolamine	12
Boric Acid	9.9
Corrosion Inhibitor	0.5
Fungicide	0.5

In order to produce a successful micro-emulsion using paraffinic oil, the amount of emulsifiers has to be increased by up to 20 – 30 % above the original formulation and the amount of oil reduced. The emulsifier is five times more expensive than the base oil, which represents a costly adjustment to the formulation. As we will see later, the inability of paraffinic oil to form emulsions is actually advantageous for the purposes of the research in this report.

2.4.3 Destabilization of Oil Emulsions via Hardness

All fluid types are tested for hard-water stability because of the progressive increase in hard-water salts in the used fluid, viz., as the fluid evaporates. Only water molecules are removed, leaving behind water salts containing calcium and magnesium. Carry-out of the fluid on the machined parts also depletes the fluid volume. As more water and fluid concentrate is added, more salts accumulate in the tank. Calcium and magnesium cations build up in the fluid. In soluble oils, the sodium sulfonate emulsifier reacts to form calcium sulfonate. This destabilization of the emulsion causes oil separation and loss of fluid concentration, see Figure 2.8 (Greeley et al., 2004). In synthetic fluids, hard-water stability problems are visible as soap scum formation on the surface of the fluid. Typically, anionic additives may have hard-water stability problems, whereas nonionic-type additives are stable to hard-water salts (Byers, 1994).

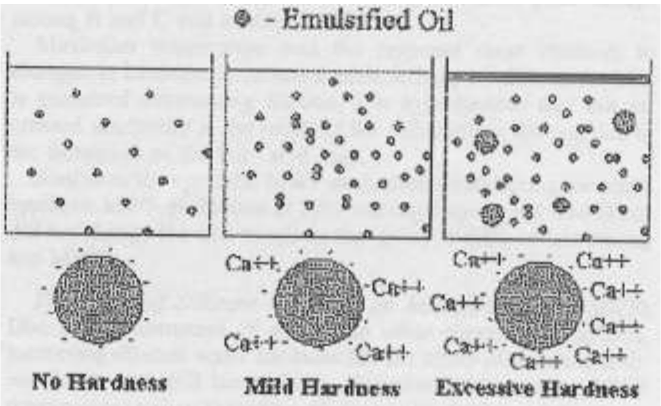


Figure 2.8. Oil Coagulation as Hardness Increases (Greeley et al., 2004).

In treatment of wastewater, oil-water emulsions of varying sizes, concentration, and potencies need to be treated to form an effluent suitable for discharge (Greeley et al., 2002). To create such an effluent the emulsified oil droplets must be removed from suspension. Because these droplets are too small to be easily removed by physical means, the preferred method employed is emulsified oil destabilization via coagulation/flocculation until droplets are of a size that can be filtered (Benito et al., 1999).

Emulsified oils, as found in semi-synthetic MWFs, are in a stable state because of the presence of ionic surfactants at the oil-water interface. These ions give the oil particles a large, negative zeta potential (a measure of the attractive force between two objects) and keep them equidistantly separated from one another. Unfortunately, the preferential use of ionic surfactants, due to cost considerations compared to nonionic surfactants, renders these emulsions liable to disruption by charge neutralization by divalent cations, such as calcium. When hardness ions are added to the solution, there is an associated increase in electrolyte concentration. These electrolytes bind ionic surfactant sites at the oil-water interface and thus the absolute value of the zeta potential of emulsified oil droplets is lowered. As zeta potential approaches zero, oil droplets are more prone to come in contact with one another and coagulate, forming larger droplets. As this process continues, the oil separates completely from the water phase and forms a cream layer on the water's surface that can be easily removed (Rios et al., 1998).

Research has shown that hardness concentration, harness ion type, temperature, and MWF composition all influence the degree and speed of oil coagulation (Bennett, 1974; Rios et al., 1997). Generally, as the concentration of hardness ions increases, so does the degree of coagulation. This trend is more pronounced for ions of bivalent metals such as calcium than for monovalent metals such as sodium (Polyanskov et al., 1986). Higher temperatures also increase the speed and degree of coagulation due to the increase in Brownian motion as oil droplets heat up (Rios et al., 1997). To prevent such destabilization, formulations incorporate chelating agents. Other factors such as freeze-thaw stability of the concentrate demand incorporation of other organics. As a result, there is a considerable amount of soluble organics in the water phase. The presence of soluble organics encourages prolific bacterial growth in these solutions. Biocides are therefore incorporated to control bacterial growth.

Research has been conducted to better understand emulsion destabilization mechanisms that lead to MWF deterioration and disposal so that MWF formulations could be designed for increased longevity (Zimmerman et al., 2004). They investigated the impact of pH and a wide range of hard water salts on MWF emulsion stability. While expected trends from the emulsion science literature were observed, it was shown that MWF destabilization can lead to an increase in the microbial load that the MWF can sustain while improving manufacturing performance as measured by the tapping torque test. Experimental observations also indicated that these trends were strongly correlated with increased emulsion particle size, regardless of whether increased particle size was achieved by aging, by reductions in pH, or by the addition of hard water salts. While some MWFs are formulated with EDTA to avoid emulsion destabilization due to cation accumulation, the study showed that EDTA can be ineffective or highly inefficient for this purpose due to direct interactions between EDTA and the MWF emulsifier system. Given the ineffectiveness of EDTA and commonly utilized MWF emulsifier systems to maintain stable emulsion size in the presence of high concentrations of hard water salts, a more effective and environmentally friendly technology is needed.

2.5 MWF Performance Evaluation Methods

2.5.1 Tapping Torque Methodology

A common MWF evaluation performance method is the tapping torque test. The tapping process has been commonly used to evaluate MWFs because it is simple, fast, inexpensive; has high precision; and tests under severe conditions (Ladov, 1973). Tests are conducted using machines such as the Microtap Megatap G8 Thread Tapping Machine, seen in Figure 2.9. This machine is specifically designed as a tapping-based MWF functionality evaluation test-bed, incorporating internal monitoring of required torque and the feature of not applying a feed to the tap, using the draw of a rotating tap to drive the vertical movement. This eliminates the possibility of speed/feed mismatches, which can have significant effects on tapping torque (Greeley et al., 2003).

Figure 2.9. Tapping Torque Machine (Greeley et al., 2003).

According to ASTM D 5619, the tapping torque tests measures the torque required to tap a thread in a blank specimen nut while lubricated with a metal removal fluid compared with the torque required to tap a thread in a blank specimen with a reference fluid. A typical tapping torque curve is shown in Figure 2.10. The ratio of the average torque values of the reference oil to the metal removal fluid tested, when using the same tap, is expressed as the percent efficiency of the fluid. The efficiency of two or more fluids can be compared when the average torque values of the reference fluid on different taps are considered to be statistically equivalent (ASTM, 2005).

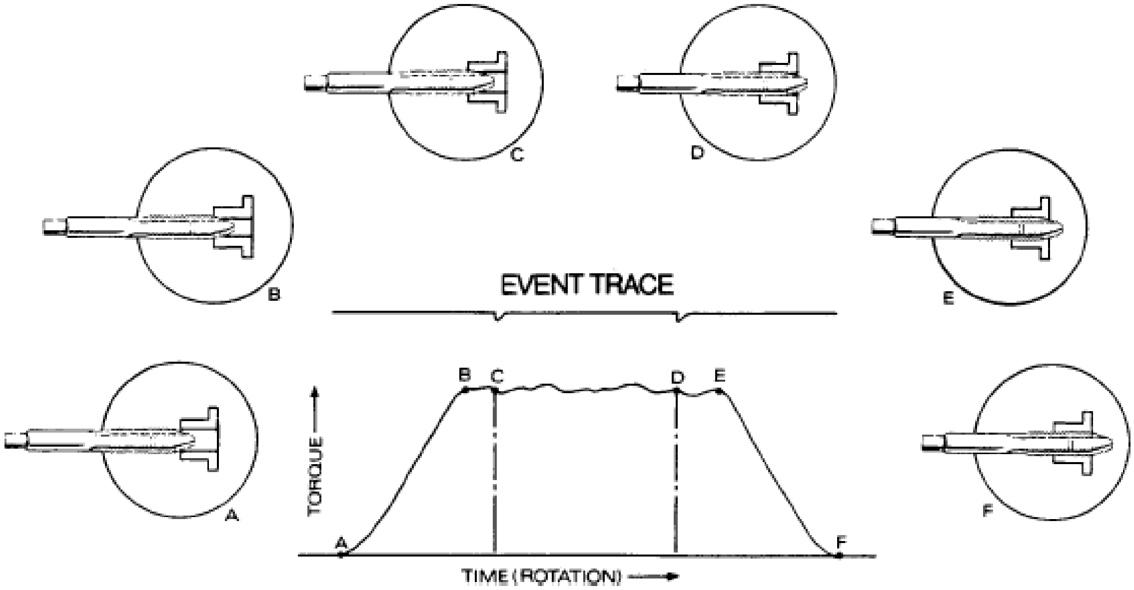


Figure 2.10. Tapping Torque Curve (insets show position of tap in specimen blank) (ASTM, 2005).

The tapping torque methodology does not appear to have the repeatability of measurements needed to make accurate MWF assessments. Additionally, temperature acquisition in tapping is believed to be very difficult, hence cooling functionality assessments cannot be made by recording temperatures (Greeley et al., 2002).

2.5.2 Drilling-Based Methodology

The true litmus test of MWF performance is the lubrication and cooling functionality of the fluid. The tapping test measures torque during tapping and therefore tends to focus on lubrication functionality. In an effort to consider both lubrication and cooling, Greeley et al. (2003) developed a drilling test methodology. Using a Mori-Seki TV-30 Light Milling/Drilling/Tapping Machine, force measurements were made using a Kistler dynamometer (Type 9272) and temperature was measured by means of an iron/constantan (t-type) thermocouple secured in the oil hole pathway of the drill located approximately 0.5 millimeters below the flank face of the drill behind the cutting edge. The set-up is shown in Figure 2.11. The thermocouple was calibrated in an ice bath, at room temperature, and in boiling water. The temperature signal was transferred off the rotating drill to a signal conditioner by a four-brush slip ring (Fabricast Model 1984).

Advantages of thermocouples include simple construction; ease of remote measurement; flexibility in construction; simplicity in operation and signal processing; and low cost.

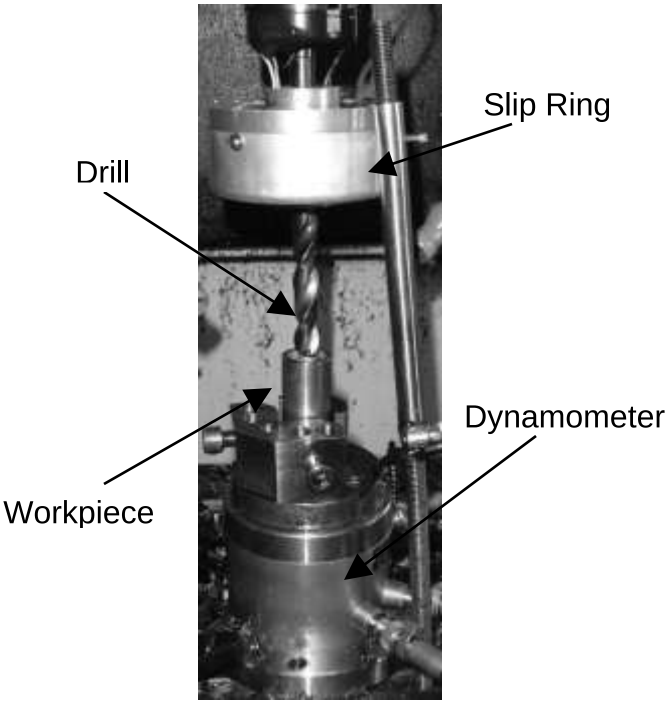


Figure 2.11. Drilling Testbed.

The drilling tests were done using a 12.7 mm diameter HSS oil hole drill with 118° point angle, 33° helix, a notched point and a 1.07 mm chisel edge. The workpiece material was a 25.4 mm diameter by 63.5 mm long blank of 1018 steel. Prior to experimentation, the workpieces and drill were rinsed with acetone to remove machining oils and contaminants. Also, to simulate wear conditions before actual testing, new drills were used to drill fifty (50) 12.7 mm deep holes in 1018 steel using a semi-synthetic MWF.

To conduct evaluations of multiple fluids in one experiment, it was necessary to avoid the use of a central fluid reservoir because it is difficult and time consuming to convert from one test fluid to the next. Therefore, a 19.05 mm diameter by 19.05 mm deep counterbore was machined into the workpieces to allow for a pool of test solution to surround the drill and to be applied to the cutting zone by flood. The drill passes through the fluid pool when cutting, which maintains wet drilling conditions.

To eliminate the possibility of fluid carry-over from one test to the next, the drill was cleaned with acetone. In the tests, 3.175 mm diameter pilot holes were used to eliminate indentation/extrusion effects of the chisel edge allowing selective acquisition of temperatures and forces generated along the drill’s cutting edge. During testing, the drill operated at the cutting speed and feed rate of 30.32 m/min and 135mm/min, respectively. The holes were drilled 12.7 mm deep.

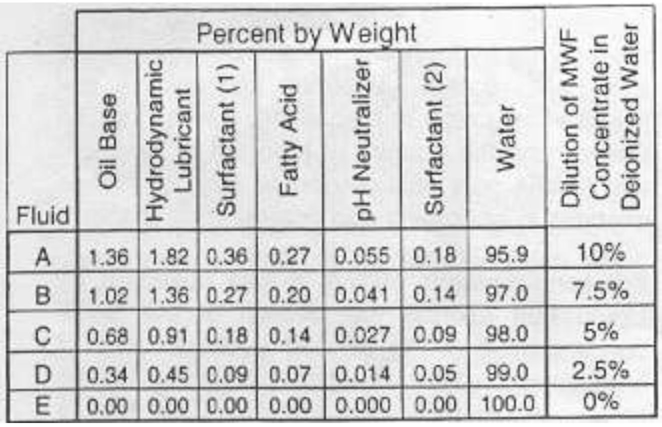
Torque and thrust data are defined as the average of the respective cutting forces during the time the drill was fully engaged in the workpiece, approximately 3.75 seconds. Temperature data are the maximum observed temperatures during the drilling cycle. In evaluating all of the solutions, six replicate holes were drilled in a randomized order using each fluid treatment and both cutting forces and cutting temperatures were recorded.

2.5.3 Comparison between Tapping Torque and Drilling-Based Methodology

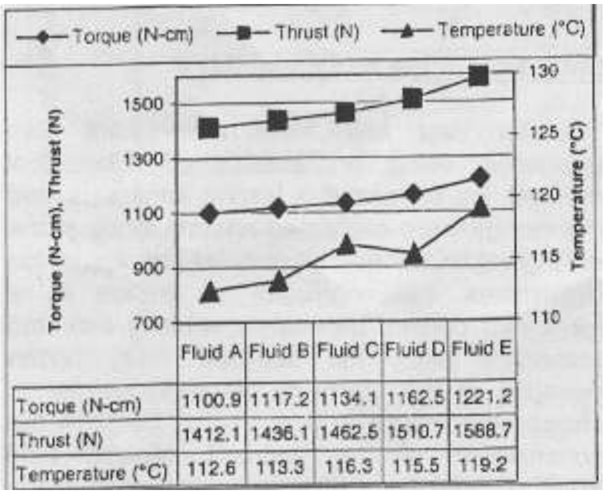
Greeley et al. (2003) also reported on the use of both laboratory/tribologically-based and machining/process-based testing for the evaluation of the performance of MWFs. Tribological tests consist of mechanical testing of a physical property such as the coefficient of friction or the size of the wear scar by methods such as tribometer or four-ball tests. These tests can offer insight into the lubricating performance of the MWF being evaluated, but their results do not always correlate well to actual MWF performance during machining. Additionally, tapping-based and tribological MWF evaluation methods do not assess MWF cooling functionality (Greeley et al., 2003).

Evaluations using the drilling-based methodology and the tapping torque test were conducted on semi-synthetic MWFs. MWF concentrate was decreased in four steps from normal concentration to none (Fluid E is DI water, see Table 2.4). Figure 2.12 contains the data from the drilling-based evaluation and Figure 2.13 contains the data from the tapping torque test.

Table 2.4. Semi-Synthetic Test Fluids (Greeley et al., 2003).



	Percent by Weight							
Fluid	Oil Base	Hydrodynamic Lubricant	Surfactant (1)	Fatty Acid	pH Neutralizer	Surfactant (2)	Water	Dilution of MWF Concentrate in Deionized Water
A	1.36	1.82	0.36	0.27	0.055	0.18	95.9	10%
B	1.02	1.36	0.27	0.20	0.041	0.14	97.0	7.5%
C	0.68	0.91	0.18	0.14	0.027	0.09	98.0	5%
D	0.34	0.45	0.09	0.07	0.014	0.05	99.0	2.5%
E	0.00	0.00	0.00	0.00	0.000	0.00	100.0	0%



	Fluid A	Fluid B	Fluid C	Fluid D	Fluid E
Torque (N-cm)	1100.9	1117.2	1134.1	1162.5	1221.2
Thrust (N)	1412.1	1436.1	1462.5	1510.7	1588.7
Temperature (°C)	112.6	113.3	116.3	115.5	119.2

Figure 2.12. Drilling-Based Evaluation Data (Greeley et al., 2003).

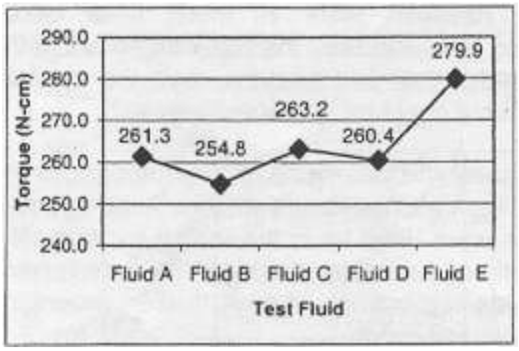


Figure 2.13. Tapping Torque Evaluation Data (Greeley et al., 2003).

It was found from this data that the cutting forces in the drilling test-bed were sensitive to 25% changes in the lubricant composition for the MWF. The results also show that applying a tapping torque test detects only gross differences in the composition of the MWF, e.g. 100% loss of lubricant.

2.6 Chapter Summary

As stated in Chapter 1, the primary focus of this research was to formulate transiently stable MWFs that are comparable to semi-synthetic and soluble oils, which represent 80% of all water soluble MWFs in the U.S. market. It was found from the literature survey that the changeover to carbide machine tools and increased machining speeds created the need for water soluble MWFs. The reason the aqueous phase was introduced is because both carbide and increased speeds cause an increase in heat generation. Thus, the water in the MWF is used to transfer the heat away in a manner that the oil could not.

The surfactants used in nearly all MWFs are critical components in terms of surface tension reduction. The HLB system (hydrophile/lipophile balance) was detailed in this chapter. It deals with selecting the correct balance between having an affinity for water versus oil for the MWF concentrate. HLB values can range from 2 to 18. A low HLB number corresponds to surfactants that are more oil-soluble while a high HLB number indicates a more water soluble surfactant. An HLB number of 14 or above indicates dispersion or solubility in water.

The different lubrication regimes were researched in the literature to see how each regime reduces friction. It was found that the hydrodynamic regime relies upon viscosity to provide lubrication. The EP additive provides chemical lubrication at higher temperatures. Finally, the boundary lubricant relies on the properties of the surfaces in motion. As will be discussed in subsequent chapters, this research project first investigated the viscous properties of the hydrodynamic regime and then moved on to classification of the remaining two. The independent classification of each regime had not been conducted previously.

Emulsion stability is extraordinarily important to MWF functionality, but, as has been discussed in this chapter, there are many factors that act to destabilize the emulsion. Destabilization can occur from ionic charge destabilization, from the base oil used in the concentrate, and also from the water used to dilute the concentrate. Not only is stability difficult to maintain, but it also creates difficulties in water treatment. Therefore, discarding one of the fundamental paradigms of current day formulations – the need for highly stable emulsions – presents the opportunity to produce MWFs that are inherently simple to formulate and maintain.

There have been a number of studies done on the functionality, emulsion stability, and microfiltration of different types of MWFs. However, no formal investigation or quantification of a surfactant's effect upon heat transfer while machining has been carried out with a MWF. Nor has experimentation revealed the effect of differing surface tensions on machining temperatures. Investigation is also needed on how changes in viscosity affect the hydrodynamic layer and, in turn, the temperatures generated. Also, all three lubrication regimes must be independently classified. Furthermore, the functionality of a transiently stable emulsion needs to be investigated. Finally, in testing the functionality of a MWF to transfer heat and reduce friction, it is important that separate experimentations are conducted to evaluate each aspect thoroughly.

Chapter 3

Effect of Water Phase Surface Tension and Viscosity on Metalworking Fluid Functionality

In this chapter, the investigations on the intrinsic properties of a metalworking fluid (MWF) for temperature reduction and lubrication, i.e., surface tension and viscosity, are discussed. The link between these fluid properties and the functionality of the MWF was examined in terms of cutting forces and machining temperature. Testing was carried out on an instrumented drilling test-bed to evaluate the effect of surface tension and viscosity on cutting temperatures and forces. This chapter first introduces the experimental design, which includes the selection of the chemicals used to vary the surface tension and viscosity of the MWF. The experimental test bed is also described. The experimental results are then presented, followed by a discussion and interpretation of the results.

3.1 Experimental Design

Experimental investigations were undertaken to evaluate the effect of surface tension and viscosity on machining temperatures and cutting forces. In separate experimentation, the role of inversely soluble lubricants in friction reduction and associated temperature reduction was investigated by looking at cutting forces and machining temperatures.

3.1.1 Surface Tension Experimental Fluids

The effect of surface tension on heat transfer in MWFs was tested with fluids that contain varying concentrations of surface tension-reducing ethers and surfactants. The control fluid for these experiments was deionized (DI) water. A glycol ether was used as the surface tension-reducing vehicle in the initial testing because it provided a means to evaluate the heat transfer properties of fluids with varying surface tensions without affecting other properties of the DI water. Surfactants, a more common additive found in MWF, were used to lower the surface tension and validate the results of the glycol ether testing. These were used in follow-up work when formulating MWFs. Surfactants are advantageous because the concentration needed to lower surface tension is quite small in comparison to ether.

The chosen ether and surfactants provide the needed surface tension reducing capabilities while not affecting other properties. Dowanol PnP was chosen over other glycol ethers because of its ability to both lower the surface tension and hold other water properties constant (Byers, 1994). This ether was particularly favorable since it reduced the surface tension to sufficiently low levels with small concentrations.

Nonionic surfactants from the Neodol family were also used to lower the surface tension in an effort to compare to and validate the ether data. Surfactants with a moderately high cloud point and intermediate hydrophile/lipophile balance (HLB number) were chosen in order to avoid potential precipitation of surfactant while assuring water dispersibility. The cloud point is the temperature at which the surfactant starts to form larger aggregates that scatter light and turn the solution cloudy. As discussed in Chapter 2, a low HLB number corresponds to surfactants that are more oil-soluble while a high HLB number indicates a more water soluble surfactant. An HLB number of 14 or above indicates complete dispersion or solubility in water. Surfactants with HLB numbers in the intermediate range of 10-14 were used in this study for their increased water solubility. Table 3.1 lists these properties for the surfactants chosen.

The Dowanol PnP and Neodol were evaluated at varying concentrations in DI water to provide for a range of surface tension values. Table 3.2 gives the concentrations used and the surface tension associated with each mixture. Pure water has a surface tension value of 72 mN/m. The range of surface tension values was fairly wide, but the values were somewhat limited by the chemicals used to lower the surface tension.

Table 3.1. Properties of Surfactants.

Chemical	**Cloud Point**	**HLB Number**
Neodol 91-6	52 °C	12.4
Neodol 91-8	80 °C	13.9

Table 3.2. Concentration of Chemicals and Corresponding Surface Tensions.

% Concentration in DI Water	**Dowanol PnP**	**Neodol 91-6**	**Neodol 91-8**
0.0001%	X	62	X
0.001%	X	53	54
0.01%	X	33	37
0.1%	X	29	30
5%	44	X	X
9%	37	X	X
16.67%	30	X	X
20%	29	X	X
30%	28	X	X
	Surface Tension (mN/m) @ 25 °C		

3.1.2 Viscosity Experimental Fluids

The viscosity of the MWFs was varied by adding UCON series non-ionic polyalklene glycol 50-HB-660 from Dow Chemical and the Pluronic series of block copolymer surfactants from BASF to DI water in varying concentrations. The copolymer surfactants used were completely soluble in water, which made it possible to produce mixtures with varying viscosities for testing purposes. These copolymer surfactants are inversely soluble, precipitating out at high temperatures to form a hydrodynamic layer affording lubrication. The cloud point plays an important role in the formation of the hydrodynamic layer. The cloud point is also referred to as the critical micelle temperature. Micelles form both when the temperature of the solution is greater than the cloud point and when the concentration of surfactant is greater than the critical micelle concentration. A higher cloud point is beneficial because the micelles will then not form prior to machining. No extreme pressure lubrication was expected from these copolymer surfactants, providing the opportunity to assess viscous lubrication alone. The control fluid in these experiments was DI water to eliminate confounding results from contaminating hardness ions.

The properties of the chemicals used in the viscosity experiments are shown in Table 3.3. All chemicals were mixed at a concentration of 2% with DI water. The viscosity of DI water at 25 °C is 0.89 cP. The viscosity of the solutions was similar to that of industrial MWFs since a concentration of 1-2% of the copolymer surfactants is commonly encountered in industrial formulations diluted for use.

3.1.3 Test Set-Up and Procedure

The drilling forces and temperature used to characterize lubrication and cooling functionality were determined using the drilling test methodology developed by Greeley et al. (2003) on a Mori-Seki TV-30 Light Milling/Drilling/Tapping Machine. Force measurements were made using a Kistler dynamometer (Type 9272). Temperature was measured by means of an iron/constantan (t-type) thermocouple secured in the oil hole pathway of the drill located approximately 0.5 millimeters below the flank face of the drill behind the cutting edge.

Table 3.3. Properties of Copolymer Surfactants.

Chemical	**Surface Tension (mN/m) @ 25 °C, 0.1% aqueous**	**Viscosity (cP) @ 25 °C, 2% Concentration in DI Water**
Pluronic L10	41	1.191
Pluronic L64	43	1.271
Pluronic 31R1	34	1.208
UCON 50-HB-660	38*	1.259

* Surface tension listed is for undiluted 50-HB-660, not for a 0.1% aqueous solution.

The set-up is shown in Fig. 2.11. The temperature signal was transferred off the rotating drill to a signal conditioner by a four-brush slip ring (Fabricast Model 1984). The drilling tests were accomplished using the Greely et al. (2003) methodology as presented in Section 2.5.2.

3.2 Experimental Results

The experimental results are presented, followed by a discussion and interpretation of the results. The objective was to begin to understand the mechanisms involved in cooling and friction reduction and relate the properties of the fluids directly to cutting process functionality.

3.2.1 Experimental Comparison of Glycol Ether Solutions: Surface Tension Experiments

Figure 3.1 shows the mean of the maximum cutting temperatures for the range of surface tension values for the various glycol ether solutions tested. The 72 mN/m surface tension point in Fig. 3.1 is the control, DI water. The results seem to suggest that reductions in surface tension lead to reductions in cutting temperatures.

To test for differences among the mean temperatures of the solutions, an Analysis of Variance (ANOVA) was conducted. Incorporated in the ANOVA calculations are the variance data from six replicate holes carried out for each testing condition. The ANOVA approach allows determination of statistical significance based on variation within and across testing conditions.

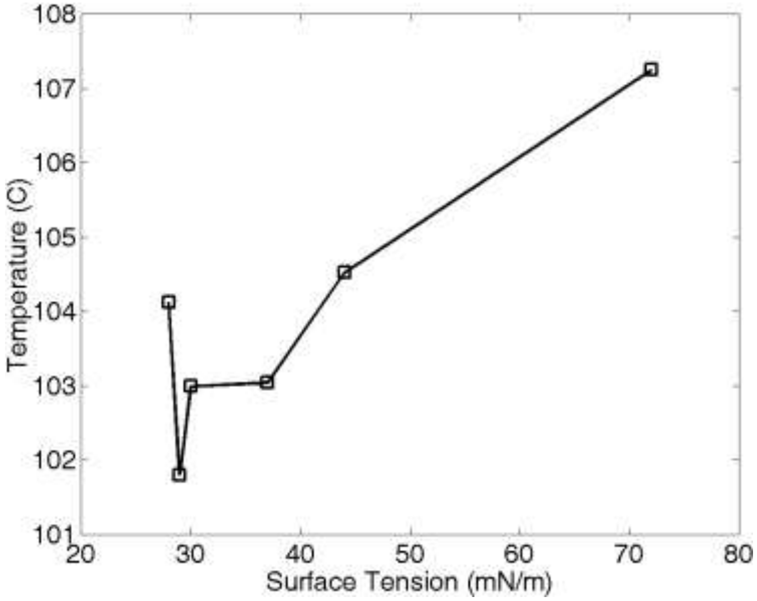


Figure 3.1. Surface Tension versus Temperature of PnP Solutions.

Table 3.4. ANOVA of Glycol Ether Solutions: Surface Tension Solution Temperatures.

Source of Variation	*SS*	*df*	*MS*	*F*	*F crit*
Mean	324221.279	1	324221.3		
Between Solutions	105.6086874	5	21.12174	8.58495	2.53
Within Solutions	73.80964316	30	2.460321		
Total	324400.6974	36			

Table 3.4 presents this analysis, with α = 0.05, for the temperatures recorded for the five levels of surface tension tested (72, 44, 37, 30, 29, and 28 mN/m). The ANOVA indicated that statistically there is reason to believe that there are real differences among the mean temperatures of the solutions for the surface tension levels tested.

To isolate the specific differences, another statistical analysis was performed using a pair-wise, two-tailed t-test with α = 0.05 on the temperatures recorded for the PnP solutions and the DI water. The analysis showed that the temperature experienced with DI water was significantly different from those of the 37, 30, 29, and 28 mN/m solutions. The 29 mN/m solution temperature was also significantly different than 44, 37, and 28 mN/m. Finally, the temperatures of the 44 and 37 mN/m solutions were deemed significantly different from each other. The results from the experiments conducted with the 28 mN/m fluid indicated that additional influences on the chemistry of the solution were being observed. Specifically, other properties besides the surface tension of the fluid were being affected, signified by the unexpected increase in temperature experienced with the 28 mN/m solution. This was most probably due to the much higher concentration of ether in this solution.

The force responses were compared in order to confirm that the solutions were similar to DI water in terms of friction reducing properties. Figure 3.2 shows the relationship between the surface tension and the torque and thrust responses. Again, the 72 mN/m surface tension point is DI water. Using a pair-wise t-test comparison, it was found that there were no significant differences among any of the PnP solutions and the DI water torque data, except between the 37 mN/m solution and DI water. There were no significant differences among the thrust responses.

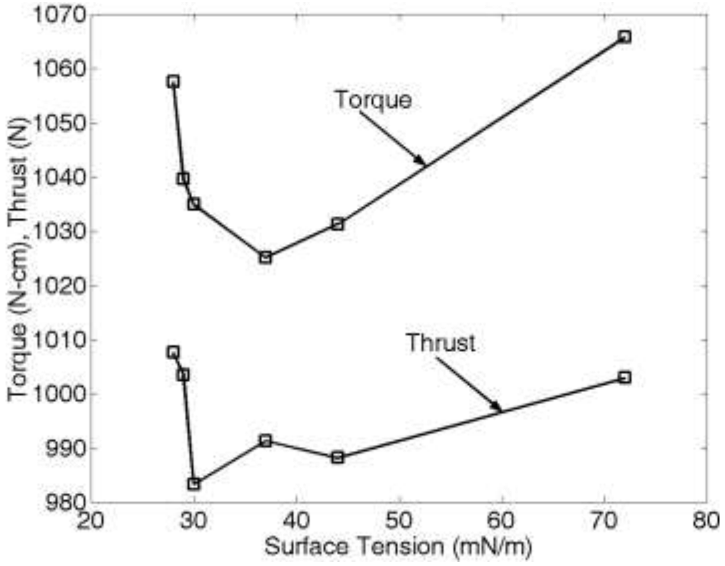


Figure 3.2. Surface Tension versus Torque and Thrust of PnP Solutions.

3.2.2 Experimental Comparison of Surfactant Solutions: Surface Tension Experiments

The concentrations of Neodol 91-6 and 91-8 used in the surface tension experiments were shown previously in Table 3.2. The concentrations used led to solutions with surface tensions similar to those obtained with the PnP solutions at the lower level but also demonstrated more modest reductions in surface tension. Figures 3.3 and 3.4 illustrate the temperature response with the different concentrations of 91-6 and 91-8, respectively. In both figures, the 72 mN/m surface tensions point is DI water. The primary effect of surface tension is expected to occur in temperature response; because of this, no torque or thrust measurements were conducted. The results seem to suggest that while sizeable reductions in surface tension lead to reductions in cutting temperatures, as was the case for the glycol ether solutions, such reductions may not occur during more modest reductions in surface tension.

Table 3.5 presents the Analysis of Variance, with $\alpha = 0.05$, for the temperatures recorded for DI water and surfactant solutions with surface tension values of 62, 54, 53, 37, 33, 30, and 29 mN/m. The ANOVA indicated that there were statistical differences among the average temperatures of the solutions for the levels tested. To isolate the specific differences, another statistical analysis was performed using a pair-wise, two-tailed t-test with $\alpha = 0.05$ on the temperatures recorded for the surfactant solutions and the DI water. The analysis showed that only the 29 and 30 mN/m solutions were significantly different than DI water. The 29 and 30 mN/m solutions (91-6 and 91-8, respectively) were significantly different from all solutions except each other.

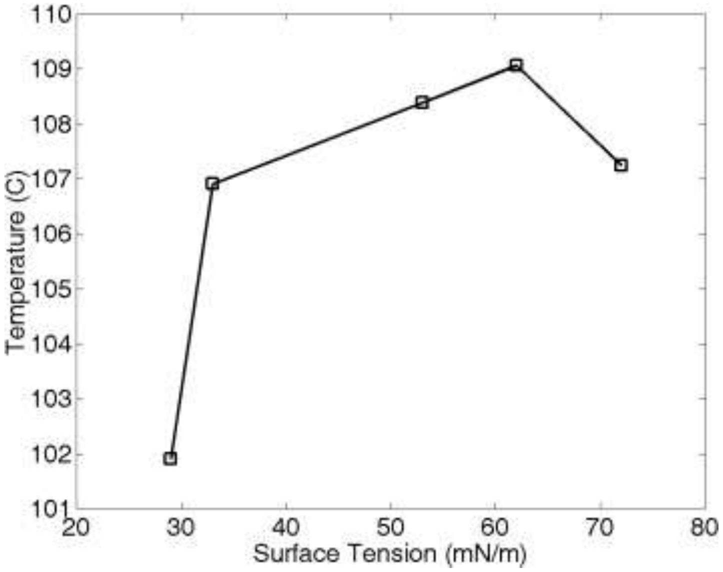


Figure 3.3. Surface Tension versus Temperature of 91-6 Solutions.

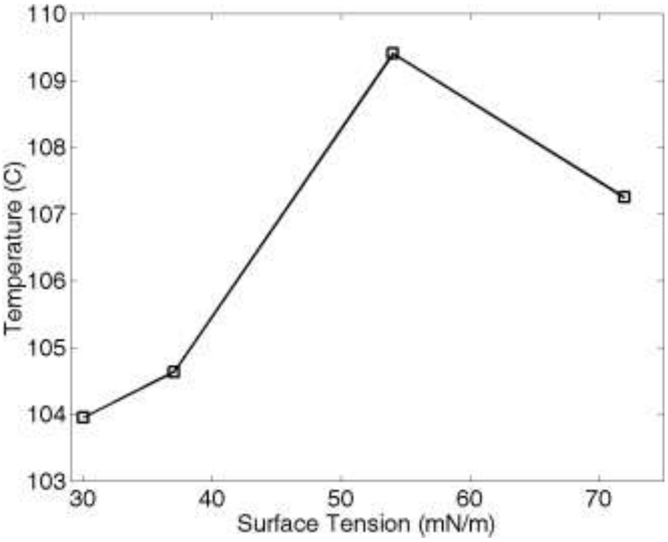


Figure 3.4. Surface Tension versus Temperature of 91-8 Solutions.

Table 3.5. ANOVA for Surfactant Solutions: Surface Tension Experiments.

Source of Variation	*SS*	*df*	*MS*	*F*	*F crit*
Mean	543837.3	1	543837.3		
Between Solutions	301.6746	7	43.09638	9.741641	2.25
Within Solutions	176.9573	40	4.423934		
Total	544316.0	48			

Figure 3.5 illustrates the similar temperature trend experienced in both the glycol ether and surfactant solutions. Statistical analysis with pair-wise t-test comparisons were used again. In this case, pair-wise, two-tailed t-tests with α = 0.05 were used to compare the temperatures of the PnP solutions against 91-6 and 91-8 with similar surface tensions. The results indicated that both types of fluids produce results with no significant differences in terms of temperature for a given surface tension.

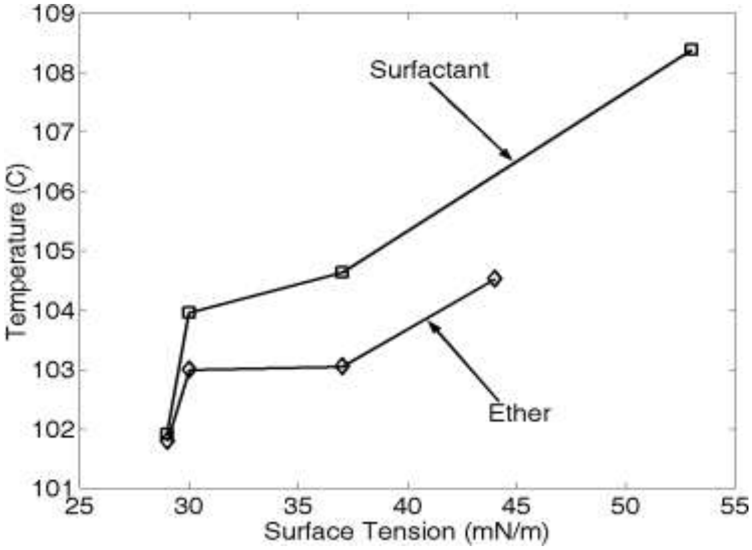


Figure 3.5. Surface Tension versus Temperature of Surface Tension Solutions.

3.2.3 Experimental Comparison of Viscosity Solutions

The average torque and thrust values of the copolymer surfactant solutions (refer to Table 3.3) are shown in Figure 3.6. The trends in the figure appear to suggest that increases in viscosity lead to decreases in torque and thrust. Additionally, when comparing Fig. 3.6 with Fig. 3.2, it is noted that the forces for the solutions with varying viscosities are lower than those for the solutions that only varied surface tension. The solutions with varying surface tensions have viscosities similar to DI water. Therefore, the reduced forces observed with the solutions with varying viscosities clearly demonstrate the friction reducing effect of increased viscosity. Statistical analysis was performed on the results of the viscosity versus cutting force experiments using a pair-wise, two-tailed t-test with α = 0.05. The solutions of 1.91, 1.208, 1.259, and 1.271 cP, (as shown in Table 3.3) were all significantly different from the DI water, but not statistically different from each other.

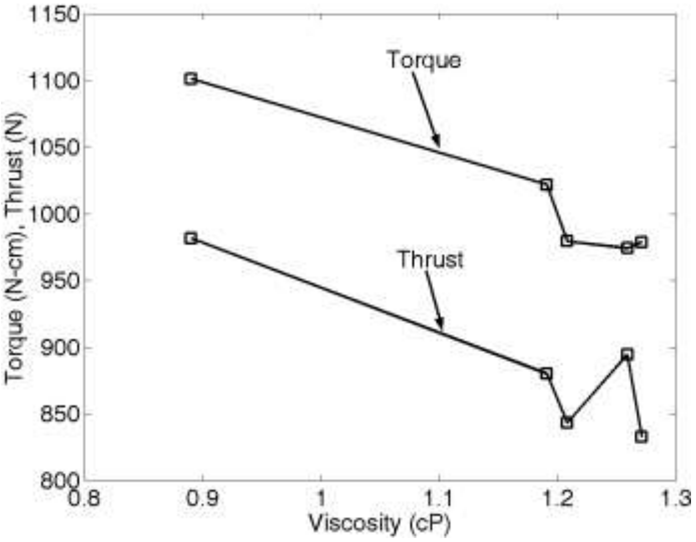


Figure 3.6. Viscosity versus Torque and Thrust of Viscous Solutions.

Figure 3.7 shows the associated temperature data. The trend in Fig. 3.7 seems to show that increases in viscosity lead to reductions in temperature. Furthermore, in comparing Fig. 3.7 with Figs. 3.1, 3.3, and 3.4, it is observed that the cutting temperature of the solution with the highest viscosity was lower than any of the temperatures with solutions that vary surface tension only. The copolymer surfactants employed in the experiments with varying viscosities have surface tensions of about 40 mN/m. This may indicate that both surface tension and viscosity effects on temperature are being observed in Fig. 3.7. The t-test comparisons done on the temperature data and the copolymer surfactant solutions were all significantly different from the DI water in terms of their cooling capability, but not statistically different from each other.

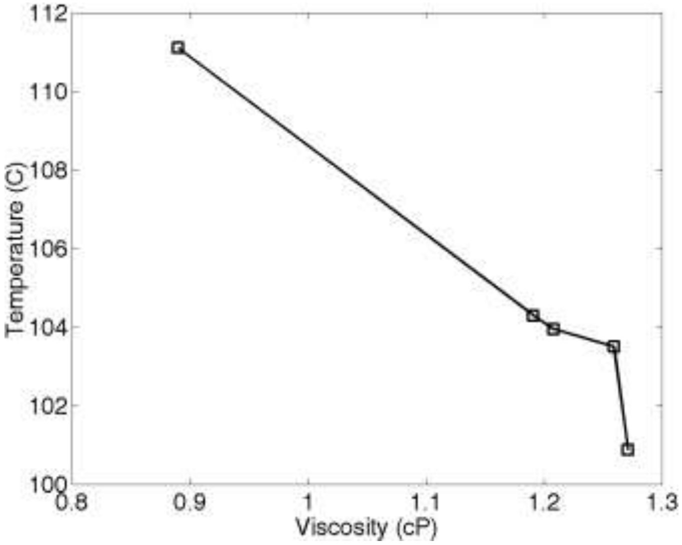


Figure 3.7. Viscosity versus Temperature of Viscous Solutions.

3.3 Discussion

The results of the surface tension investigation indicated that fluids with a lower surface tension cause reduced cutting temperatures in machining. This finding is consistent with Hetsroni et al. (2004) who studied the effect of surface tension on heat transfer during a boiling process. They explored surface tension values in the range of 30-40 mN/m and found that decreases in surface tension enhance heat transfer during a boiling process. It is hypothesized here that, as the surface tension of the fluid is decreased, the molecules become less attracted to each other. Thus, the intermolecular bonds break down and the wettability of the fluid is increased. As the wettability increases, the fluid coats the tool and workpiece more completely. The fluid is then able to transfer heat away from the area of the tool and workpiece that it is in contact with. The exception in this research is the 28 mN/m, 30% glycol ether solution, which did not follow the expected linear downward trend in terms of temperature. It is hypothesized that, with such a high concentration of glycol ether in solution, the chemistry of the DI water changed, not just the surface tension, and thus affected the cooling characteristics of the fluid.

It was noted over the range of viscosities tested here that increases in viscosity lead to both decreases in cutting forces and temperature. Viscosity is the load bearing property of a fluid or film. Viscosity has little effect on wettability, but it does have an effect on the speed at which the liquid fills the gap and the thickness of the liquid in the gap. Thus, viscosity affects the amount of MWF at the chip/tool cutting interface. Merchant (1950) found that roughly two-thirds of the power required to drive the cutting tool is consumed by deforming metal. The remaining third is consumed in overcoming chip friction. The power to deform the material is the same for a given set of cutting conditions. Therefore, since all tests run here used the same set of cutting conditions, the results indicate that the MWF solutions are reducing the friction experienced due to chip contact along the rake face and the contact of the freshly cut surface on the flank faces of the tool. This effect improves as the viscosity of the solution increases.

As the viscosity of a solution increases, the layer of hydrodynamic lubrication increases and a larger gap is created between the chip and the face of the drill. The larger gap creates less rubbing, or friction, between the chip and tool. The reduction in friction leads to a reduction in frictional heat generated. It was also noted that the solutions with varying viscosities exhibited a greater temperature decrease compared to the solutions with varying surface tensions. It should be noted that the copolymer surfactants provide both a hydrodynamic layer of lubrication and surface tension reducing effects (see Table 3.3). All of the solutions with varying viscosities have a surface tension around 40 mN/m, which indicates enhanced heat transfer properties of the fluids. This suggests that the lubrication effect and the surface tension effect have a combined influence on reducing temperatures.

Although only an inversely soluble lubrication regime has been studied here, it is acknowledged that in almost every industrial MWF, an inversely soluble lubricant is partnered with a boundary lubricant and/or an extreme pressure additive to further reduce heat generation. The testing was performed without either of these additional regimes in an effort to isolate the effect of the viscosity of inversely soluble lubricants on heat generation.

3.4 Chapter Summary

The following can be concluded from the results presented in this chapter:

1. Using ethers, experimental investigation revealed that a lower surface tension, which improves wettability, will reduce temperatures during machining.

2. In similar testing done with surfactants, the results showed that surfactants can also provide surface tension reducing properties that lead to better cooling functionality during machining.

3. In a comparative analysis of the ether and surfactant solutions, it was found that a lower surface tension, independent of the type of chemical used to lower it, provided better cooling.

4. Separate experiments with varying viscosities showed that as the viscosity of a solution increased, the cutting forces decreased. This suggests that friction between the chip/workpiece and the tool has been reduced.

5. The experiments with varying viscosities and associated low surface tensions demonstrated, through reduced cutting temperatures, the combined effects of these two fluid properties.

Chapter 4 discusses experiments conducted that focus on the extreme pressure and boundary lubrication regimes.

Chapter 4

Effect of Particle Size and Proportion of Oil on Metalworking Fluid Functionality

With the inversely soluble lubricants tested in Chapter 3, the lubrication experienced was hydrodynamic. In the experimentation discussed in this chapter, an extreme-pressure (EP) and boundary lubrication regime were explored by incorporating EP additives such as chlorinated paraffins and boundary lubricant esters into the solution. In particular, the oil phase was introduced to provide additional viscosity and lubrication to the solution, while the water phase was adjusted to optimal surface tension, as found from previous testing. Also, the effects of surface tension, particle size, and proportion of oil in the mixture on the MWF functionality were evaluated by a design of experiment (DOE) approach. Based on the DOE results, the most important factors that influence drilling temperatures and forces were identified, which in turn guided further experimentation and formulation.

4.1 Extreme Pressure Additive Experiments

The hydrodynamic lubrication regime has already been independently classified. In this study, the EP additive was assessed to identify and optimize certain important characteristics of the formulation, including particle size of the emulsion and the proportion of oil.

4.1.1 Experimental Design

Experiments were carried out with the water phase adjusted to a surface tension that ensured wetting. Prior experimentation on surface tension indicated a value below 40 mN/m would provide adequate wettability. The oil phase of the solution was comprised of an EP additive, ParOil 1057 from Dover Chemical. The variables of interest of the solution were the particle size of the emulsion, the surface tension of the aqueous phase, and the proportion of oil.

Particle Size. The particle size of the emulsion is adjusted by blending the solution for varying amounts of time. The longer a solution is blended, the more dispersed it becomes, i.e., the smaller the particle size will become. It is hypothesized that the better a solution is mixed (the smaller the particle size), the more effective it will be during machining. During drilling experimentation, solutions were used that had been mixed for varying lengths of time to achieve particle sizes of 5 or 25 microns, the low and high levels of the experiment, respectively, and the tests in each case were run within 30 seconds of mixing.

It is important that the oil and water in the solutions that are investigated have the ability to separate fairly easily since that is the basis of the transiently stable formulation. Thus, solutions were made and the stability of each was investigated. The particle size and other relevant details are presented in Table 4.1, for one particular solution. One hundred mL solutions with the following ingredients were prepared:

- 5% ParOil 1057 – extreme pressure additive (Dover Chemical)
- 0.1% Neodol 91-6 – nonionic surfactant (Shell Chemical)
- 94.9% Water – adjusted to a pH of 9 to retard corrosion and bacterial growth.

The solutions from Table 4.1 were centrifuged for 1 and 2 minutes at 3200 RPM. The solutions showed the ParOil visibly separating out after 1 minute but more complete separation was experienced at 2 minutes, as would be expected.

Surface Tension. Based upon prior experimentation in Chapter 3, the level at which surface tension will ensure good wettability and temperature reduction is 40 mN/m or less. Therefore, the solutions were adjusted by adding Neodol 91-6 to deionized (DI) water. The low level was adjusted to 30 mN/m. The high level was 72mN/m, which is the surface tension of unadjusted DI water.

Proportion of Oil. In industrial metalworking fluids (MWFs), EP additives (here, ParOil 1057) are used in a concentration range of 1-5%. Therefore, in an effort to use a similar range, the high level was 5% and the low level was 1%.

Table 4.1. Oil-Water Solutions.

Mixing time	T(initial) °C	T(final) °C	Mean particle size (µm)	Mean particle size across samples (µm)
5 minutes	20	38	5.049	4.65
			4.605	
			4.288	
2 minutes	21	38	19.96	17.87
			17.16	
			16.49	

Table 4.2. Factors and Levels Summary.

	Design Factor		
Level	Proportion (A)	Particle Size (B)	Surface Tension (C)
Low (-1)	1%	5 microns	30 mN/m
High (+1)	5%	25 microns	72 mN/m

The response variables were maximum temperature during machining in °C, torque in N-cm, and thrust in N. The drilling forces and temperature used to characterize lubrication and cooling functionality were determined using the drilling test methodology developed by Greeley et al. (2003) on a Mori-Seiki TV-30 Light Milling/Drilling/Tapping Machine. Torque and thrust data are defined as the average of the respective cutting forces during the time the drill was fully engaged in the workpiece, approximately 3.75 seconds. Temperature data are the maximum observed temperatures during the drilling cycle.

Table 4.3 provides the eight unique test settings for the experiment. The tests were conducted in a randomized order across all 16 trials, i.e., two replicates for each test condition. The results, in terms of average torque, thrust, and maximum temperature, are also given in the table.

4.1.2 Determination and Interpretation of Significant Variable Effects

To evaluate which effects were significant, 95% confidence intervals were calculated for the effects for each of the response variables. The intervals and effects are shown in Table 4.4. The confidence intervals were calculated as follows:

$$\text{Effect Estimate} \pm t_{\nu,1-\left(\frac{\alpha}{2}\right)}\sqrt{\left(\frac{4S_{PE}{}^{2}}{N}\right)}$$

ν , degrees of freedom (DOF) = 8

α , confidence interval 100(1 - α)% = 0.05

$t_{8,0.975}$, t-statistic for a 95% confidence interval with 8 DOF = 2.306

$S_{PE}{}^{2}$, pooled variance estimate for each response variable

N , total number of tests conducted = 16

Based upon the significant effects that were found from the confidence intervals, two-way diagrams were constructed to evaluate interaction effects.

Table 4.3. 2^3 Factorial Design with Associated Data Points.

2^3 Design				Avg Maximum Temp (°C)	Avg Torque (N-cm)	Avg Thrust (N)
Run	A	B	C			
1	-1	-1	-1	98.54	1073.865	1144.889
2	1	-1	-1	101.54	1023.772	1095.874
3	-1	1	-1	93.14	1054.518	1128.719
4	1	1	-1	102.14	1042.393	1104.479
5	-1	-1	1	100.94	1026.612	1093.704
6	1	-1	1	101.54	1001.488	1055.852
7	-1	1	1	99.74	1051.941	1140.095
8	1	1	1	100.34	1059.042	1127.309

Table 4.4. Confidence Intervals for Estimated Effects.

Maximum Temperature	Effect (°C)	95 % CI - Low	95% CI - High	
A-Proportion of Oil	3.3	2.45	4.15	**Significant**
B-Particle Size	-1.8	-2.65	-0.95	**Significant**
C-Surface Tension	1.8	0.95	2.65	**Significant**
AB	1.5	0.65	2.35	**Significant**
AC	-2.7	-3.55	-1.85	**Significant**
BC	0.6	-0.25	1.45	
ABC	-1.5	-2.35	-0.65	**Significant**

Torque	Effect (N-cm)	95 % CI - Low	95 % CI - High	
A-Proportion of Oil	-20.06	-37.05	-3.07	**Significant**
B-Particle Size	-20.54	-37.53	-3.55	**Significant**
C-Surface Tension	-13.86	-30.85	3.13	
AB	17.54	0.55	34.53	**Significant**
AC	11.04	-5.95	28.03	
BC	20.9	3.91	37.89	**Significant**
ABC	-1.44	-18.43	15.55	

Thrust	Effect (N)	95 % CI - Low	95 % CI - High	
A-Proportion of Oil	-30.98	-45.18	-16.78	**Significant**
B-Particle Size	27.58	13.38	41.78	**Significant**
C-Surface Tension	-14.24	-28.44	-0.04	**Significant**
AB	12.46	-1.74	26.66	
AC	5.66	-8.54	19.86	
BC	31.36	17.16	45.56	**Significant**
ABC	0.072	-14.13	14.27	

Maximum Temperature. All effects were deemed significant except the two-factor interaction between particle size and surface tension. Since the three-factor interaction, "ABC", is significant as shown in Table 4.4, main effects and two-factor interactions must be interpreted with caution. Figure 4.1a and 4.1b indicate that, regardless of the particle size and surface tension, the machining temperature increased with an increase in the proportion of oil. Moreover, at both particle sizes, the presence of a wetting agent was effective at reducing the machining temperature at the low oil concentration. This beneficial effect was lost as the proportion of oil was increased. These effects were likely the effect of two counteracting factors influencing machining temperatures – cooling and lubrication.

While lubrication is generally thought to be improved by an increase in the proportion of oil, the cooling ability will be simultaneously lowered (Byers, 1994). The machining temperature appears to be particularly sensitive to the loss in cooling properties of the

MWF with an increase in oil content. Subsequently, a fluid with a low surface tension has better wettability characteristics and is able to transfer heat away from the work piece and tool more readily. Moreover, the net effect of a combination of small particle size, which reduces the heat generated, and low surface tension, which enhances heat transfer characteristics, is that it functions better to reduce temperature.

Low particle size

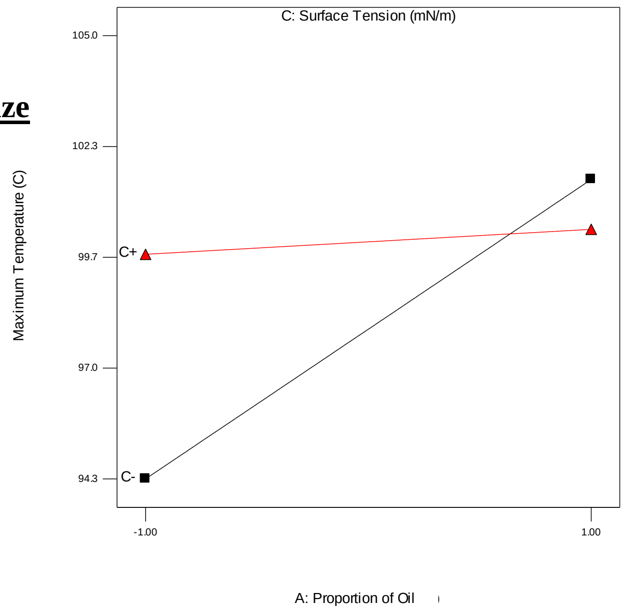


Figure 4.1a. Interaction Effect between the Proportion of Oil and Surface Tension (AC) at the Low Level of Particle Size (B). **Legend:** ■ = Low Level ▲ = High Level

High particle size

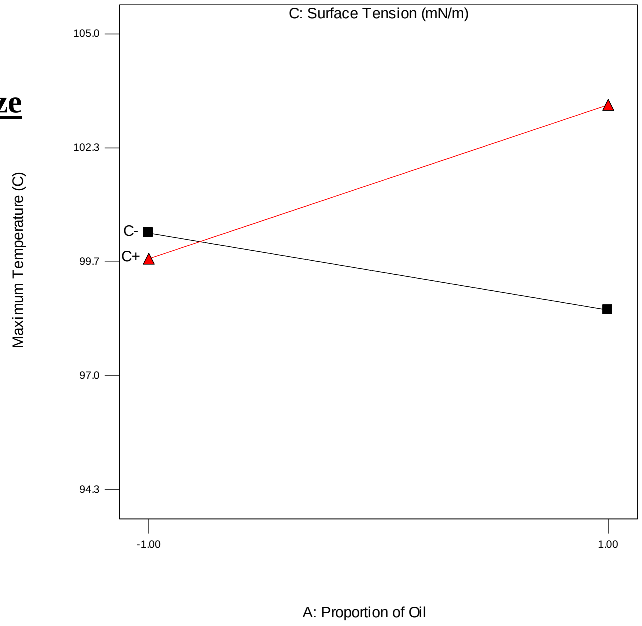


Figure 4.1b. Interaction effect between the Proportion of Oil and Surface Tension (AC) at the high level of Particle Size (B). **Legend:** ■ = Low Level ▲ = High Level

Torque. Table 4.4 shows that the two factor interaction effects “AB” and “BC” are significant. The interaction effect in Fig. 4.2 illustrates that particle size only affects the torque when the proportion of oil is high. This signifies, as expected, that any effect the particle size may have on torque will be more evident with a higher level of oil in solution. The torque will decrease with more oil in solution because it makes the solution more viscous and aids in reducing friction experienced both at the tool-workpiece interface and the tool-chip interface.

The interaction effect in Fig. 4.3 demonstrates that the particle size only has an effect on torque at high surface tension values. This coupled with Fig. 4.2 illustrates that particle size has an effect on torque when a high concentration of oil is in solution and the surface tension is high. It is reasonable that with more oil in solution the particle size of the oil would become more important to friction reduction. One explanation for why the particle size has more of an effect when the surface tension is high centers around surfactants. At a high surface tension value the solution does not contain any surfactants; therefore, the EP additive does not break down as readily into solution (form smaller particles) and may not function as well. The particles will also be prone to separate out (form large particles) without surfactants in solution.

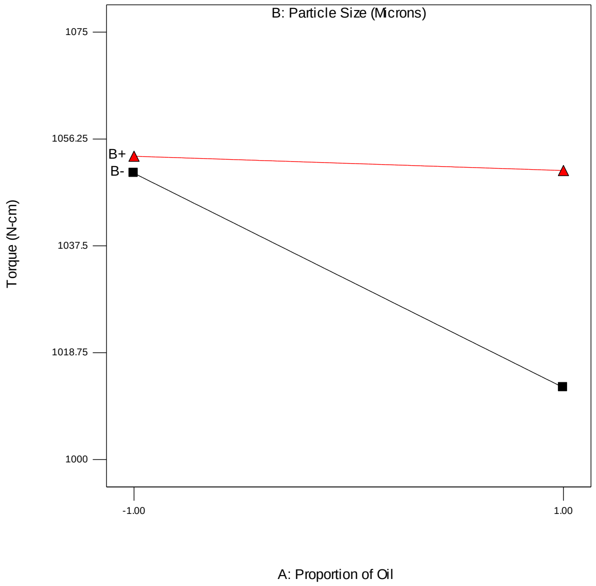


Figure 4.2. Interaction effect between the Proportion of Oil and Particle Size (AB).
Legend: ■ = Low Level ▲ = High Level

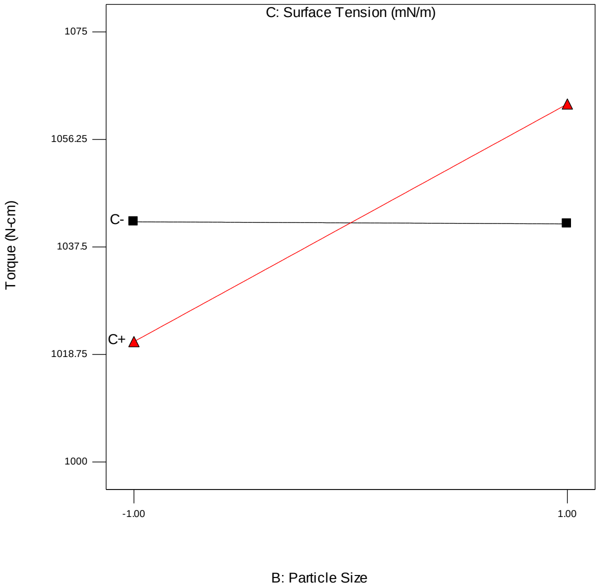


Figure 4.3. Interaction effect between Particle Size and Surface Tension (BC).
Legend: ■ = Low Level ▲ = High Level

Thrust. The effects for thrust are quite similar to those for torque. Perhaps surface tension has the most significant effect for thrust. Figure 4.4 illustrates that at a high surface tension the particle size of the solution dramatically affects the thrust.

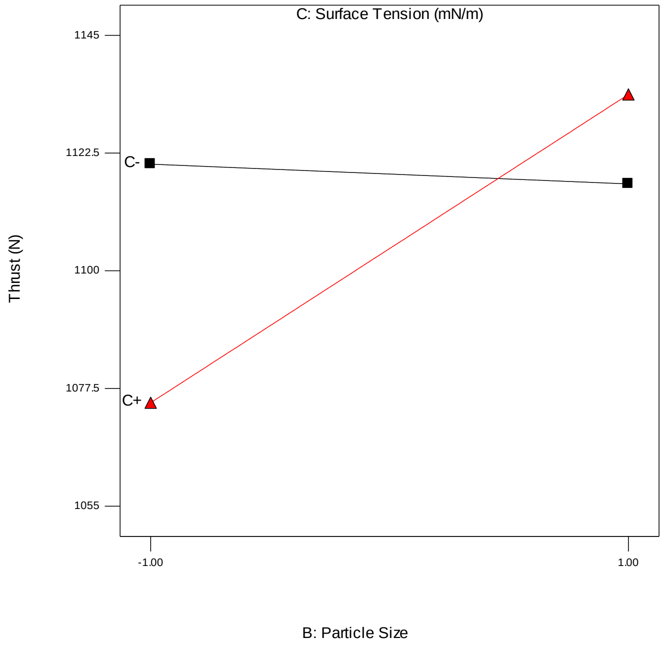


Figure 4.4. Interaction effect between Particle Size and Surface Tension (BC).
Legend: ■ = Low Level ▲ = High Level

It is interesting that surface tension has an effect on thrust because surface tension is more often correlated with temperature reduction. Yet in this experiment, a high surface tension led to a decrease in thrust values. On the other hand, when the surface tension was at the high level and there were no surfactants in solution, the particles were more prone to separate out and form larger particles.

With the EP additive being blended into smaller particles, it was able to fill interstitial gaps, between the tool and workpiece and tool and chip, which a larger particle may not have been able to penetrate, thus increasing the cooling capability of the fluid. The net effect of small particle size, which reduces the heat generated, combined with a low surface tension is that it provides better overall temperature reduction. At a high surface tension value, the particle size has more of an effect because the solution does not contain any surfactants; therefore, the EP additive does not break down as readily into solution, or form smaller particles, and may not lubricate as well.

4.2 Boundary Lubricant Experiments

The boundary lubrication regime was also evaluated by introducing a ester as the boundary lubricant. Surface tension, particle size, and amount of boundary lubricant were examined to determine the manner in which they might influence lubrication and cooling both singly and in concert. Once the optimal formulation was determined, it was compared to an industrial soluble oil MWF to assess whether the custom formulation, void of many additional surfactants and other additives, would perform similarly to that of an industrial formulation. Only the boundary lubricant formulation was compared to the industrial soluble oil because of the similar chemical characteristics of the custom formulation and the soluble oil.

4.2.1 Boundary Lubricant Selection

The boundary lubricants explored were esters from Dover Chemical. The factors that played a role in determining which esters to use were:

1. Hydrolytically stable (non-water soluble) so that they would separate out of solution;
2. A low viscosity to facilitate a small particle size;
3. A density heavier than water so that when the esters separate out of solution, they fall to the bottom of the solution.

Based on these criteria, an oil soluble boundary lubricant, Base Methyl Lardate (Base ML), was selected for further study, viz., Base Methyl Lardate (Base ML) provides methyl ester lubricity for oil soluble MWFs.

In an effort to compare the optimal boundary lubricant formulation to an industrial MWF, Trim Sol was investigated because it has similar chemical characteristics to the formulations developed. Trim Sol is a standard, general-purpose, multi-metal soluble oil MWF for machining of ferrous and nonferrous materials (TrimCoolant, 2006). It has the lubricity necessary to do heavy-duty machining center work and still provide the wetting and cooling necessary for high-speed turning and grinding operations. It has a wide application range and is used to replace straight oil on some types of screw machines. It is also easily recycled or disposed with conventional techniques and equipment.

4.2.2 Experimental Design

The variable levels for particle size, surface tension, and proportion of oil were all the same as that used for the EP additive: 5 and 25 microns in diameter, 30 and 72 mN/m, and 1 and 5% concentration, respectively. Tests were conducted using the drilling test bed developed by Greeley et al. (2003). The response variables are also the same as those used for the EP additive: maximum temperature during machining in °C, torque in N-cm, and thrust in N.

Table 4.5 provides the (8) unique test settings for the experiment. The tests were conducted in a randomized order across all (16) trials, i.e., two replicates for each test condition. The results in terms of average torque, thrust, and maximum temperature are also given in the table.

Table 4.5. 2^3 Factorial Design with Associated Data Points.

Design Factor			
Level	Proportion (A)	Particle Size (B)	Surface Tension (C)
Low (-)	1%	5 microns	30 mN/m
High (+)	5%	25 microns	72 mN/m

Test	A	B	C	Avg Torque (N-cm)	Avg Thrust (N)	Avg Max Temp (°C)
1	-1	-1	-1	1106.93	1163.80	95.84
2	1	-1	-1	1061.11	1111.75	97.04
3	-1	1	-1	1115.13	1171.10	97.04
4	1	1	-1	1062.22	1107.86	94.94
5	-1	-1	1	1093.50	1159.47	97.04
6	1	-1	1	1060.56	1098.25	98.54
7	-1	1	1	1085.09	1140.26	96.74
8	1	1	1	1059.37	1123.58	100.34

4.2.3 Determination and Interpretation of Significant Variable Effects

Table 4.6 gives estimates of the variable effects; both main effects and interaction effects are presented for each of the three responses. To evaluate which effects were significant, 95% confidence intervals were calculated about the effect estimates for each of the response variables based on the replication of the experiment. The confidence intervals were calculated in the same manner as the confidence intervals for the EP additive study.

Table 4.6. Confidence Intervals for Estimated Effects

Max. Temperature	**Effect (°C)**	**95% CI - Low**	**95% CI - High**	
A-Proportion of Oil	1.05	-0.14	2.24	
B-Particle Size	0.15	-1.04	1.34	
C-Surface Tension	1.95	0.76	3.14	**Significant**
AB	-0.30	-1.49	0.89	
AC	1.50	0.31	2.69	**Significant**
BC	0.60	-0.59	1.79	
ABC	1.35	0.16	2.54	**Significant**

Torque	**Effect (N-cm)**	**95% CI - Low**	**95% CI - High**	
A-Proportion of Oil	-39.35	-43.55	-35.14	**Significant**
B-Particle Size	-0.07	-4.28	4.14	
C-Surface Tension	-11.72	-15.93	-7.51	**Significant**
AB	0.03	-4.18	4.24	
AC	10.02	5.81	14.23	**Significant**
BC	-4.73	-8.94	-0.52	**Significant**
ABC	3.58	-0.63	7.79	

Thrust	**Effect (N)**	**95% CI - Low**	**95% CI - High**	
A-Proportion of Oil	-48.30	-61.36	-35.24	**Significant**
B-Particle Size	2.38	-10.68	15.44	
C-Surface Tension	-8.24	-21.30	4.82	
AB	8.34	-4.72	21.40	
AC	9.35	-3.71	22.41	
BC	0.68	-12.38	13.74	
ABC	13.93	0.87	26.99	**Significant**

Maximum Temperature. Table 4.6 shows that the three-factor interaction (ABC) for maximum temperature is significant. Therefore, the significant main effects and two-factor interactions must be interpreted with caution. The interaction effect in Fig. 4.5 shows the two-way diagrams for the two-factor interaction (AC) at both the low and high levels of variable B – particle size. The data in Figure 4.5a indicate that when the particle size was low, the effect of surface tension on the maximum temperature was the same regardless of the proportion of oil, viz., reductions of surface tension decreased the maximum temperature. Figure 4.5b indicates that when the particle size was large and the proportion of oil was high, a lower surface tension value led to a lower maximum temperature. Figure 4.5b also indicates that at a high particle size and low proportion of oil, changes in surface tension had a small effect on the maximum temperature. The lowest maximum temperature occurred when particle size was large, the proportion of oil was at its high level, and surface tension was at its low value.

As has been shown previously, the aqueous phase of a MWF is used for cooling, while the oil phase is used for lubrication, or friction reduction. Therefore, a fluid with a low surface tension has better wettability characteristics and is able to transfer heat away from the workpiece and tool more readily.

Low particle size

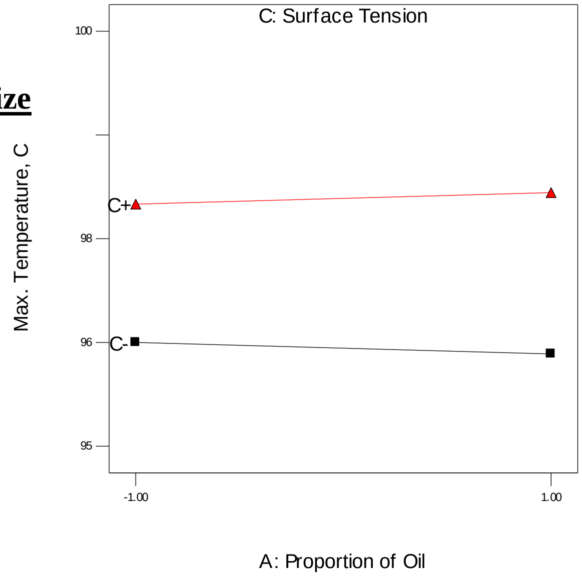


Figure 4.5a. Interaction effect of Proportion of Oil and Surface Tension (AC) at the low level of Particle Size (B). **Legend:** ■ = Low Level ▲ = High Level

High particle size

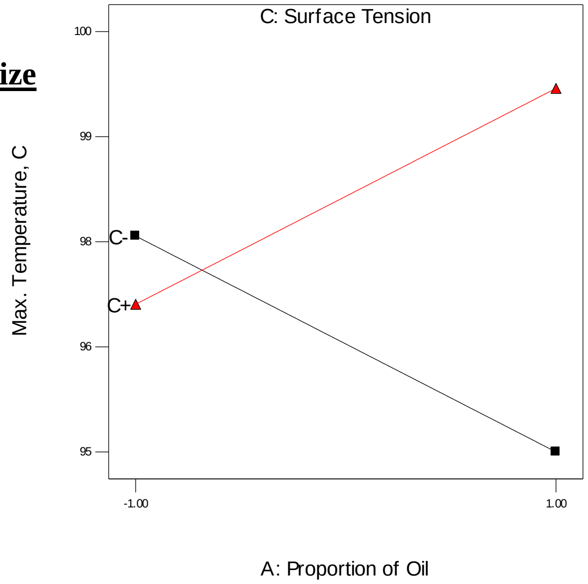


Figure 4.5b. Interaction effect of Proportion of Oil and Surface Tension (AC) at the high level of Particle Size (B). **Legend:** ■ = Low Level ▲ = High Level

Torque. Table 4.6 shows that the two-factor interaction effects on torque, “AC” and “BC”, are significant. The interaction effect in Fig. 4.6 shows that regardless of the surface tension, a larger proportion of oil lowered the torque. Figure 4.6 also illustrates that the surface tension of the solution had a greater effect on the torque when the proportion of oil was low but the torque values were higher. The torque will decrease with more oil in solution because it makes the solution more viscous and aids in reducing friction experienced both at the tool-work piece interface and the tool-chip interface.

The interaction effect in Figure 4.7 demonstrates that while the particle size does not have much of an effect on the torque, a larger particle size does increase the effect of surface tension. In both Figs. 4.6 and 4.7 it should be noted that a higher surface tension produced a lower torque value, regardless of the proportion or particle size of the oil. At a high surface tension value the solution does not contain any surfactants; therefore, the boundary lubricant does not break down as readily into solution, which may lead to lower torque. The particles will also be prone to separate out, or form large particles, without surfactants in solution. This finding is in direct opposition to what was seen with the EP additives. The important discovery from this surface tension phenomenon was that the boundary lubricants were actually performing better in terms of friction reduction at a higher surface tension value. This is novel because with a higher surface tension value, or without surfactants, the boundary lubricant will separate out of solution more readily.

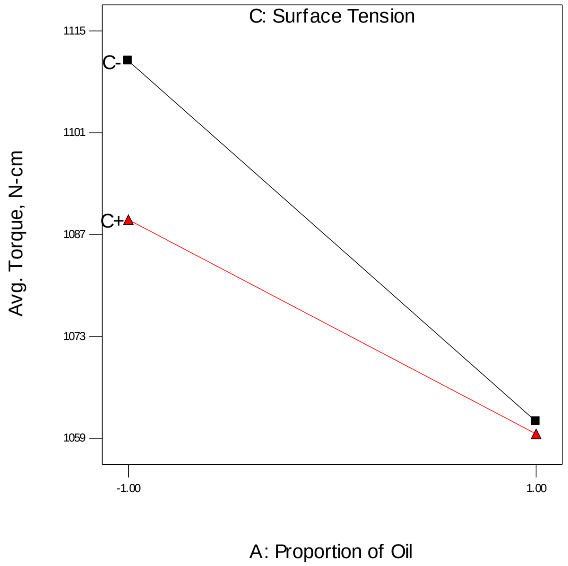


Figure 4.6. Interaction effect of Proportion of Oil and Surface Tension (AC).
Legend: ■ = Low Level ▲ = High Level

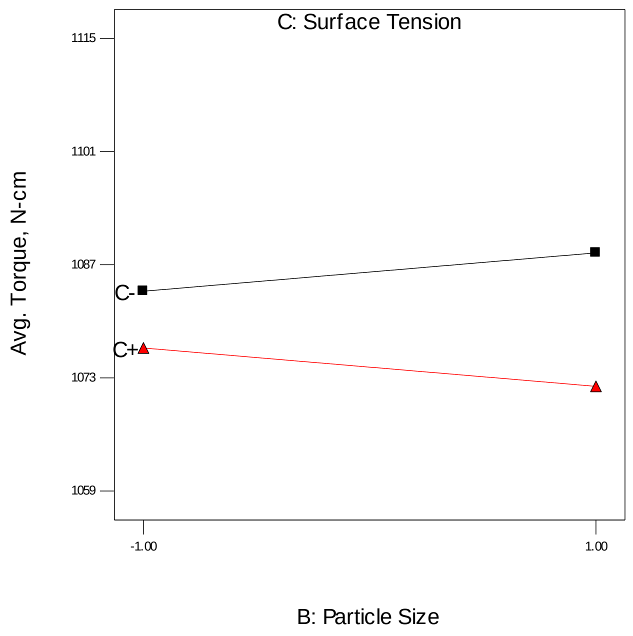


Figure 4.7. Interaction effect of Particle Size and Surface Tension (BC).
Legend: ■ = Low Level ▲ = High Level

Thrust. The interaction effects shown in Figures 4.8a and 4.8b indicate that regardless of the surface tension or the particle size, a high proportion of oil led to lower thrust values. However, Figure 4.8b also shows that with a larger particle size the effect of surface tension of the fluid was significant with lower surface tension producing significantly lower thrust values.

Figures 4.8a and 4.8b illustrate an accepted fact - that with more lubricant in solution, there will be better friction-reducing properties. Figures 4.6, 4.8a, and 4.8b all seem to indicate that a 1% solution of the boundary lubricant is insufficient for good MWF performance.

Low particle size

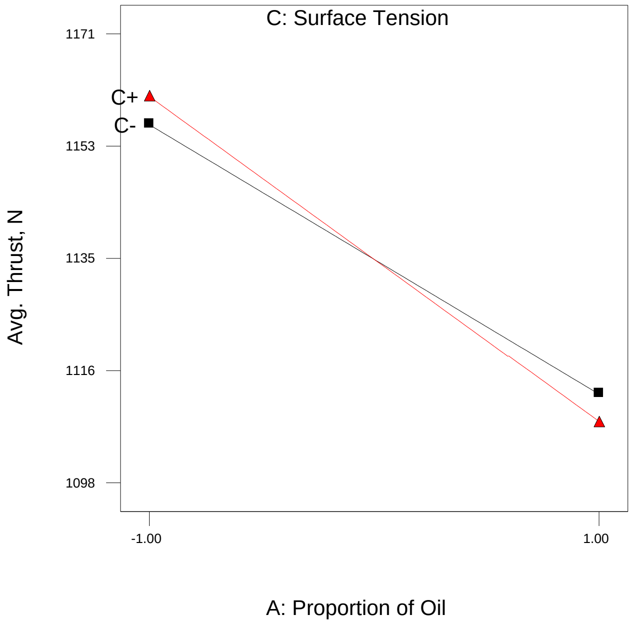


Figure 4.8a. Interaction effect of Proportion of Oil and Surface Tension (AC) at the low level of Particle Size (B). **Legend:** ■ = Low Level ▲ = High Level

High particle size

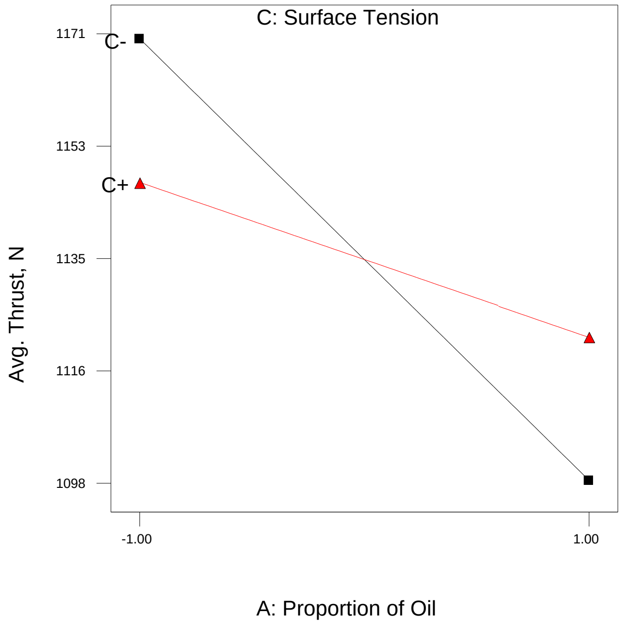


Figure 4.8b. Interaction effect of Proportion of Oil and Surface Tension (AC) at the high level of Particle Size (B). **Legend:** ■ = Low Level ▲ = High Level

4.2.4 Comparison of Optimal Boundary Lubricant Formulation with an Industrial Metalworking Fluid

It was concluded from the DOE that the boundary lubricant formulation with a high proportion of oil, a large particle size, and a low surface tension exhibited the best cooling and lubrication. To compare this optimal boundary lubricant formulation to an industrial MWF, five replicates of both the optimal formulation and Trim Sol at 5% concentration were run in a randomized order. The average response values and their standard deviations are presented in Table 4.7.

In an effort to compare the optimal boundary lubricant fluid to an industrial formulation, t-tests with $\alpha = 0.05$ were performed on the torque, thrust, and temperatures recorded for the Trim Sol solution and the boundary lubricant fluid. The t-tests showed no statistical difference between the Trim Sol and the optimal boundary lubricant formulation fluid in terms of torque and thrust. This finding indicates that the lubricity capabilities of the optimal boundary lubricant are comparable to an industrial formulation. However, the maximum temperature t-test showed a statistical difference between the Trim Sol and the optimal boundary lubricant formulation fluid. This could be due to the fact that industrial formulations have other additives that aid in cooling (Bittorf, 2007). Future formulations incorporating all lubrication regimes may compare more favorably in terms of cooling.

Table 4.7. Results of Industrial MWF and Optimal Formulation Tests.

Fluid	**Average**	**Standard Deviation**
Trim Sol (5%)		
Torque (N-cm)	1034.42	16.07
Thrust (N)	1090.61	19.57
Max Temp (C)	87.49	2.06
Optimal Formulation		
Torque (N-cm)	1024.42	39.98
Thrust (N)	1064.93	43.84
Max Temp (C)	94.45	1.43

4.3 Chapter Summary

1. With the EP additive being blended into smaller particles, it was able to fill interstitial gaps, between the tool and workpiece and tool and chip, which a larger particle may not have been able to penetrate, thus increasing the cooling capability of the fluid.

2. The net effect of small particle size, which reduces the heat generated, combined with a low surface tension is better overall temperature reduction.

3. At a high surface tension value the particle size has more of an effect because the solution does not contain any surfactants; therefore, the EP additive does not break down as readily into solution, and may not lubricate as well.

4. With the boundary lubricant, the lowest maximum temperature occurs when particle size is large, the proportion of oil is at it high level, and surface tension is at its low level.

5. The boundary lubricants performed better in terms of friction reduction at a higher surface tension value, or without surfactants, meaning that the boundary lubricant will separate out of solution more readily than the surfactants.

6. The lubricity capabilities of the optimal boundary lubricant formulation were comparable to an industrial formulation; however, the cooling capability of the boundary lubricant formulation was found to be inferior to the industrial MWF.

Chapter 5

Formulation and Investigation of Custom Two-Phase Metalworking Fluids

This chapter focuses on the development of transiently stable custom MWF formulations. The customized MWF formulation was developed using the results of the design of experiments (DOEs) for the extreme pressure (EP) additive and boundary lubrication regimes of the last chapter. Investigations were done on the MWF emulsion stability characteristics and the time for the oil to separate out. The custom formulations were validated and compared to industrial MWFs using machining functionality tests.

5.1 Factor Levels for Custom Formulation

Based on the DOE results, the most important factors that influence drilling temperatures and forces were identified, which in turn guided the custom formulation. Associated work was also done to optimize the custom formulations using the DOE data from the previous chapter.

5.1.1 Factor Levels for the EP Additive Regime

In Chapter 4, using an EP additive, the following factors and levels were studied with a DOE approach:

1. Proportion of oil in solution
   Low – 1% oil, High – 5% oil

2. Particle size of emulsion
   Low – 5 microns, High – 25 microns (diameter)

3. Surface tension
   Low – 30 mN/m @ 25 °C (0.1% Neodol 91-6 in solution), High – 72 mN/m @ 25 °C (No surfactant added).

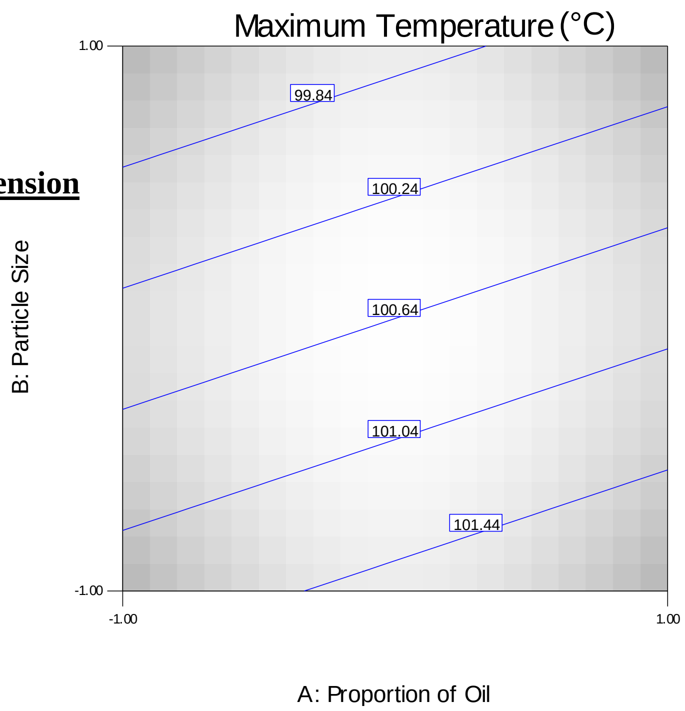
Based on the results of the design of experiment (2^3 factorial), the following prediction equations, in terms of coded factors (± 1), were developed:

$$MaximumTemperature = 99.74 + 1.65A - 0.90B + 0.90C + 0.75AB - 1.35AC - 0.75ABC$$

$$AverageTorque = 1041.70 - 10.03A + 10.27B + 8.77AB + 10.45BC$$

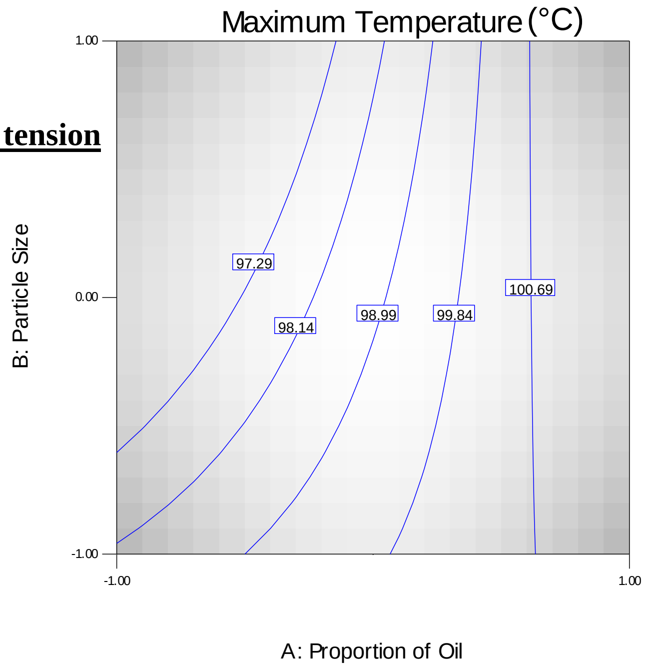
$$AverageThrust = 1111.37 - 15.49A + 13.79B + 15.68BC.$$

These equations were used to create contour plots for the temperature and force responses. Figures 5.1a and b are contour plots for maximum temperature, Figures 5.2a and b are contour plots for average torque, and Figures 5.3a and b are contour plots for average thrust.



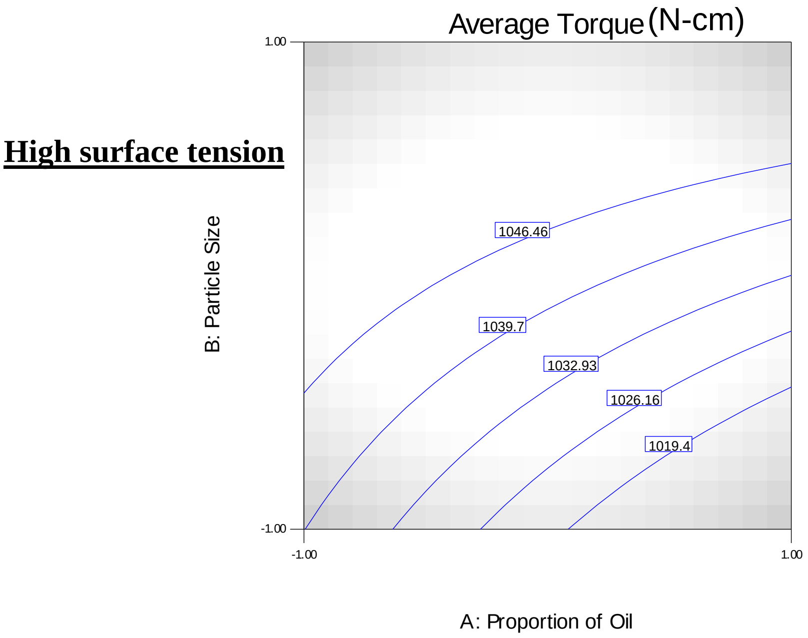
High surface tension

Figure 5.1a. Contour plot of Proportion of Oil and Particle Size (AB) at the high level of Surface Tension (C) for Maximum Temperature.



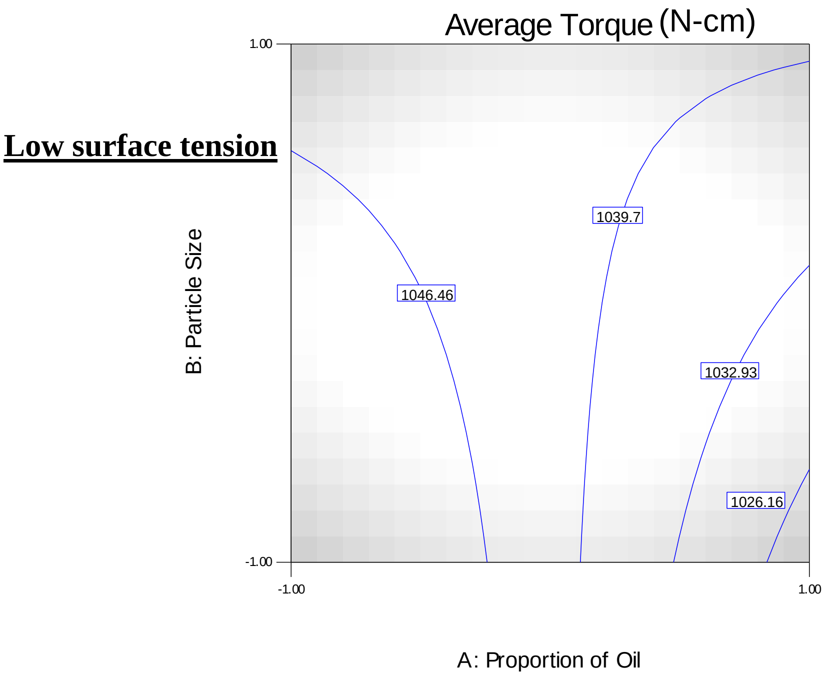
Low surface tension

Figure 5.1b. Contour plot of Proportion of Oil and Particle Size (AB) at the low level of Surface Tension (C) for Maximum Temperature.



High surface tension

Figure 5.2a. Contour plot of Proportion of Oil and Particle Size (AB) at the high level of Surface Tension (C) for Average Torque.



Low surface tension

Figure 5.2b. Contour plot of Proportion of Oil and Particle Size (AB) at the low level of Surface Tension (C) for Average Torque.

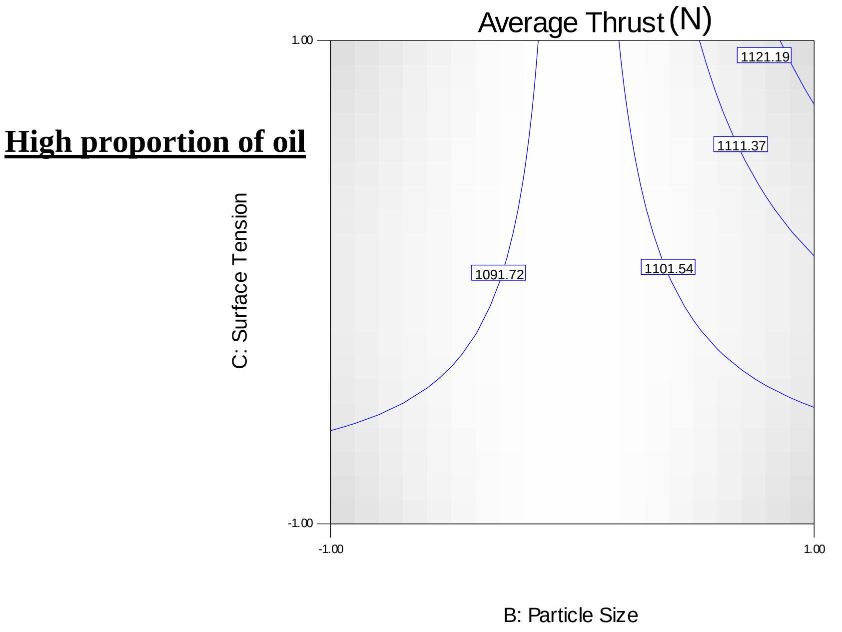


Figure 5.3a. Contour plot of Particle Size and Surface Tension (BC) at the high level of Proportion of Oil (A) for Average Thrust.

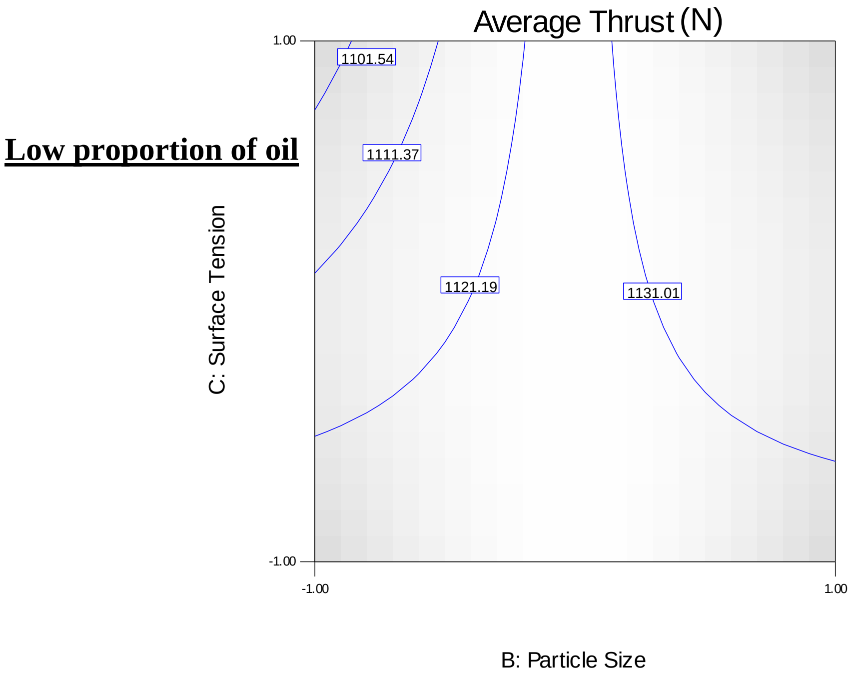


Figure 5.3b. Contour plot of Particle Size and Surface Tension (BC) at the low level of Proportion of Oil (A) for Average Thrust.

The contour plots indicate that the lowest maximum temperature was experienced with a low surface tension level, a low proportion of oil, and a large particle size. Yet the contour plots for both torque and thrust indicate that force reduction was greatest with a high surface tension level, a large proportion of oil, and a small particle size. Each of these conclusions follows the same, traditional logic that is used in formulating industrial MWF. It has been proven that fluids with lower surface tension values are better at transferring heat away from the workpiece and tool, thus enhancing the cooling capabilities of the fluid. Also, it is well known that the oil phase provides lubrication, whereas the water phase of the fluid is used for cooling. Therefore, the higher the proportion of oil in the fluid, the better it will be at friction reduction but the worse it will be at cooling.

The best cooling characteristics of the fluid will come at a cost to lubrication and vice versa. Therefore, to balance these conflicting effects, the surface tension, which has been found to affect the cooling characteristics, was adjusted to a level that is the best for cooling. Whereas, the particle size and proportion of oil, which have more of an impact on lubrication, were adjusted to a level that was determined to be the best for friction reduction.

Table 5.1 shows the performance predictions for these factor levels, i.e., a 5% proportion of oil, a 5 micron particle size, and a 30 mN/m surface tension. Using these factor levels, the predicted maximum temperature was higher than that predicted with a low level of oil in solution. Hypothetically, it was higher because there was more oil in solution which decreased the cooling capability of the fluid. It should also be noted that better lubrication was experienced because of the increase from 1% to 5% oil in solution.

Table 5.1. Performance Predictions for the EP additive.

	Prediction	**SE Mean**	**95% CI low**	**95% CI high**
Maximum Temperature (°C)	101.24	0.79	91.15	111.32
Average Torque (N-cm)	1023.08	11.48	986.54	1059.62
Average Thrust (N)	1097.76	9.87	1070.34	1125.19

5.1.2 Factor Levels for the Boundary Lubrication Regime

In Chapter 4, using a boundary lubricant, the same factors and levels listed above for the EP additive were studied with a DOE approach. Based on the results of the DOE, the following prediction equations, in terms of coded factors (± 1), were developed:

$$MaximumTemperature = 97.19 + 0.97C$$

$$AverageTorque = 1080.49 - 19.67A - 5.86C + 5.01AC$$

$$AverageThrust = 1134.51 - 24.15A.$$

These equations were used to create the following contour plots of the temperature, torque, and thrust responses. Figure 5.4 is a contour plot for maximum temperature, Figure 5.5 is a contour plot for average torque, and Figure 5.6 is a contour plot for average thrust.

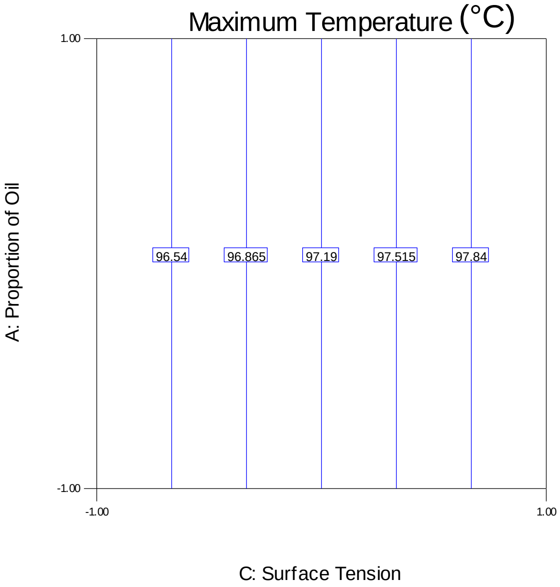


Figure 5.4. Contour plot of Surface Tension (C) for Maximum Temperature.

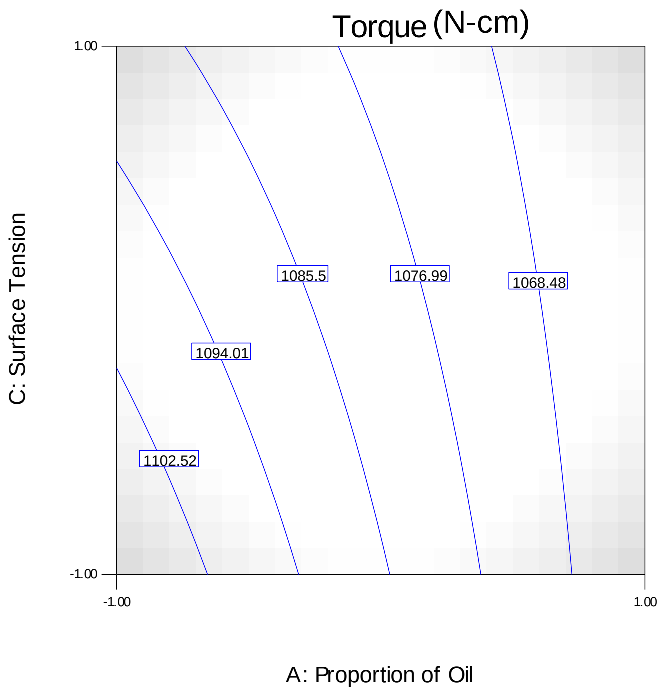


Figure 5.5. Contour plot of Proportion of Oil and Surface Tension (AC) for Average Torque.

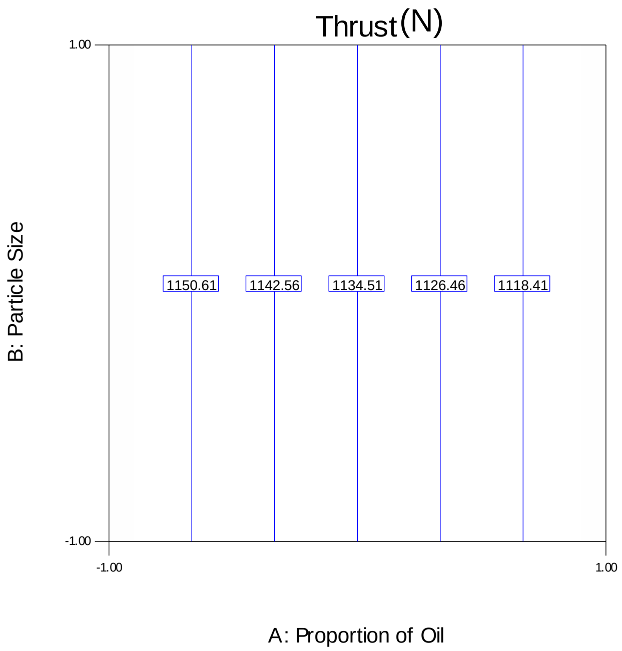


Figure 5.6. Contour plot of Proportion of Oil (A) for Average Thrust.

The contour plots indicate that the lowest maximum temperature was experienced with a low surface tension level, independent of the proportion or particle size of the oil. The contour plots for both torque and thrust show that force reduction was greatest with a high proportion of oil for both torque and thrust and a high surface tension value for torque. These conclusions indicate that the particle size is of little importance when using a boundary lubricant. However, a small particle size was chosen for the performance prediction because this is the size that was best for the EP additive and will be used in the custom formulation. The surface tension, which has been found to affect the cooling characteristics of a MWF more dramatically than the lubrication characteristics, was adjusted to a level that was the best for cooling. Finally, since it was found that a higher proportion of oil in solution was advantageous to lubrication and did not affect cooling, a high level was used for this factor.

Table 5.2 shows the performance predictions for these factor levels, viz., a 5% proportion of oil, a 5 micron particle size, and a 30mN/m surface tension. In both the EP additive and boundary lubricant testing, it was found that a 5% proportion of oil, a 5 micron particle size, and a 30 mN/m surface tension provided the most favorable cooling and lubrication properties from the fluids. The customized formulation was developed using these factor levels.

5.2 Particle Size and Oil Separation of Custom Formulation

To determine the viability of the custom formulations, two crucial elements of a transiently stable emulsion were assessed. The particle size is investigated to ensure the correct size was produced. The separation characteristics, which are an important aspect of transiently stable emulsions, were examined to make certain that the oil and water phases will split into two separate parts.

5.2.1 Particle Size

The focus of this research project was to develop a two-phase mixture that is functionally comparable to industrial MWF and easily separates into separate oil and water streams. Therefore, the custom formulation was developed to have good cooling and lubrication functionality and separation ability. To achieve the required cooling and lubrication functionality, the water phase surface tension was adjusted to a level adequate for cooling and all three lubrication regimes were employed, similar to an industrial MWF.

Table 5.2. Performance Predictions for the Boundary Lubricant.

	Prediction	**SE Mean**	**95% CI low**	**95% CI high**
Max. Temperature (°C)	96.13	0.62	94.39	97.88
Avg. Torque (N-cm)	1059.30	2.30	1051.95	1066.64
Avg. Thrust (N)	1112.64	5.99	1096.01	1129.28

A formulation without the surface tension adjusted was also prepared to investigate particle size and separation kinetics of a fluid void of surfactants. The initial formulations were composed of the following components:

Custom Formulation 1 – Surface Tension Unadjusted (72mN/m)
1% ParOil 1057 (EP additive)
2% Maylube E-112 (Boundary lubricant)
2% UCon 50-HB-660 (Inversely soluble hydrodynamic lubricant)
95% DI water

Custom Formulation 2 - Surface Tension Adjusted (30mN/m)
1% ParOil 1057 (EP additive)
2% Maylube E-112 (Boundary lubricant)
2% UCon 50-HB-660 (Inversely soluble hydrodynamic lubricant)
0.1% Neodol 91-6
94.9% DI water.

Prior to machining tests, the custom formulations were studied in terms of particle size and oil separation characteristics. In previous testing it was determined that a lower surface tension fluid is able to create smaller particle sizes. Thus, in this particle size testing, different mixing times were employed on the higher surface tension fluid, Custom Formulation 1, to study how long the solution needed to be blended to obtain an adequately small particle size. The objective was to determine the minimum mixing time to get the particle size to 5 microns or smaller. Table 5.3 indicates the particle diameter of Custom Formulations 1 and 2 for different mixing times.

It appeared from the above data that there may be additional influences on particle size besides just the mechanical energy of the blender. In Table 5.3, the particle size was expected to continue to decrease as the mixing time increased, yet the data did not exhibit this linear relationship. It was hypothesized that when all three lubrication regimes were used concurrently, there were unnoticed chemical interactions affecting the particle size. To investigate this phenomenon, the same solutions - Custom Formulations 1 and 2 - were blended for 5 minutes and then allowed to sit for 24 hours (to allow ample time for any chemical reaction to take place). Finally, they were mixed for the time indicated. Table 5.4 presents the results of this study for Custom Formulations 1 and 2.

Table 5.3. Custom Formulations 1 and 2 particle diameter for different mixing times.

Mixing Time	Diameter (μm)
Custom Formulation 1	
15 seconds (Replicate 1)	3.38
15 seconds (Replicate 2)	2.82
1 minute	3.30
5 minutes	2.53
Custom Formulation 2	
15 seconds	2.61

Table 5.4. Custom Formulations 1 and 2 particle diameter for different mixing times after being allowed to sit for 24 hours.

Mixing Time	Diameter (μm)
Custom Formulation 1	
15 seconds	2.94
1 minute	2.48
Custom Formulation 2	
15 seconds	2.15
1 minute	1.80

As anticipated, the results from this investigation indicated that as mixing time was increased, there was a decrease in particle size. Thus, it is important to allow the solutions to sit for 24 hours before experimentation. It also shows that to achieve the necessary particle size, 5 microns or less, the solution only needs to be mixed for approximately 15 seconds.

5.2.2 Oil Separation

One of the important characteristics of two-phase mixtures is their ability to separate into oil and water streams. The separation characteristics of Custom Formulations 1 and 2 were investigated based on a 100 mL sample, of which 5 mL was oil. To expedite the separation process, they were centrifuged for 1.5 minutes at 3200 RPM in a conical test tube. One mL of the ParOil and 2 mL of the MayLube separated out of the Custom Formulation 1 that had been mixed for 15 seconds. Determination of the oil types was accomplished through visual analysis of sample layering. Approximately 0.5 mL of the ParOil and 1 mL of the MayLube separated out of the Custom Formulation 2 that had been mixed for 15 seconds. In both Custom Formulations that had been mixed for 1 minute, 2 mL of MayLube and 0.5 mL of ParOil separated out of solution. The solutions that had been mixed for 5 minutes had no visible evidence of oil separation. Table 5.5 summarizes the results.

Table 5.5. Oil Separation Results.

	Time Mixed		
	15 seconds	**1 minute**	**5 minutes**
CF 1	~2 mL Maylube and ~1mL ParOil separate out	~2 mL MayLube and ~0.5 mL ParOil separate out	No visible evidence of oil separation
CF 2	~1 mL Maylube and ~0.5 mL ParOil separate out	~2 mL MayLube and ~0.5 mL ParOil separate out	No visible evidence of oil separation

Note: No UCon separation was visible.

The UCon was not separating out of any of the solutions, which was not acceptable for the purposes of this fluid. So to aid in the separation process, duplicate samples were heated in a 70 °C water bath for several hours to exaggerate the effect of increased temperatures (higher temperatures would likely produce the same result in much less time). After this heating cycle a notable separation occurred (as determined through visual observation) indicating that there was the potential to separate the UCon out of solution as well when heat is applied.

5.3 Machining Tests of Custom Formulations

It was determined from the particle size and oil separation studies that it is possible to achieve the necessary particle size and that the oil and water will readily separate. Now that the efficacy of the formulations had been confirmed, it was appropriate to evaluate the functionality of the fluids.

5.3.1 Initial Machining Tests

The custom formulations were run along with two industrial fluids, Castrol 6519 and Trim E206nd, at a 5% concentration and DI water (the DI water is used as a benchmark). The custom formulations were mixed for 5 minutes then allowed to sit, undisturbed, for 24 hours, then mixed again for 15 seconds and tested. This produced solutions with particle sizes of approximately 2-3 microns. The drilling forces and temperature used to characterize lubrication and cooling functionality were determined using the drilling test methodology developed by Greeley et al. (2003) on a Mori-Seiki TV-30 Light Milling/Drilling/Tapping Machine. All fluids were tested five times and were run in a randomized order. Table 5.6 presents the average and standard deviation of these tests.

Pair-wise, two-tailed t-tests with $\alpha = 0.05$ were performed on the torque, thrust and temperature responses between fluids. In each category (torque, thrust, and temperature) the mean values of the Trim and 6519 were found to be not different. The means of the custom formulation and the custom formulation with surfactant were found to be not different. All other t-tests between means indicated that the fluids were different. Table 5.7 summarizes the t-test results.

The t-tests indicate that the custom formulations were reducing friction better than the industrial fluids because the torque and thrust values, for both custom formulations, were significantly less than those for both industrial fluids. Although the friction reduction was better with the custom formulation, the temperature reduction properties were worse than the industrial fluids. The results are somewhat contradictory considering that Custom Formulation 2 contains the Neodol surfactant at a concentration that has been proven to reduce the surface tension to a point that enhances the cooling characteristics to a level similar to an industrial fluid. Yet, the surface tension results were with the water phase alone, so there is the potential that the oil phase of the custom formulations was affecting the cooling characteristics and not allowing adequate heat transfer. More investigation of this was needed as noted in the next section on the temperature reduction properties of the custom formulations.

Table 5.6. Initial Custom Fluid Machining Test Results.

Fluid	**Average**	**St. Deviation**
DI H2O		
Average Torque (N-cm)	1130.47	15.25
Average Thrust (N)	1202.36	23.51
Max Temp (C)	99.02	2.13
6519 (5%)		
Average Torque (N-cm)	1072.75	23.75
Average Thrust (N)	1138.4	32.77
Max Temp (C)	89.17	1.17
Trim E206nd (5%)		
Average Torque (N-cm)	1065.06	14.70
Average Thrust (N)	1124.46	12.33
Max Temp (C)	87.61	1.30
Custom Formulation 1		
Average Torque (N-cm)	951.89	17.32
Average Thrust (N)	988.66	42.17
Max Temp (C)	93.13	1.53
Custom Formulation 2		
Average Torque (N-cm)	960.04	12.50
Average Thrust (N)	1012.1	19.25
Max Temp (C)	93.85	0.98

Table 5.7. t-Test Results for Initial Machining Tests.

t-Test Between Means	**Torque**	**Thrust**	**Temperature**
DI versus 6519	Different	Different	Different
DI versus Trim	Different	Different	Different
DI versus Custom 1	Different	Different	Different
DI versus Custom 2	Different	Different	Different
6519 versus Trim	Not Different	Not Different	Not Different
6519 versus Custom 1	Different	Different	Different
6519 versus Custom 2	Different	Different	Different
Trim versus Custom 1	Different	Different	Different
Trim versus Custom 2	Different	Different	Different
Custom 1 versus Custom 2	Not Different	Not Different	Not Different

5.3.2 Reformulation and Functionality Testing

Both Custom Formulations 1 and 2 contained 5% oil, and both solutions did not perform comparably in terms of cooling characteristics to the industrial MWFs. The water phase of the fluid provides the cooling, therefore in the reformulations the overall proportion of oil in solution is reduced to 1%. The custom formulations with 1% oil in solution, Custom Formulations 3 and 4, were formulated with the same hydrodynamic lubricant as Custom Formulations 1 and 2. The reformulations with 5% oil in solution, Custom Formulations 5 and 6, used paraffinic oil as the hydrodynamic lubricant. The paraffinic oil was used in this case because it is commonly used as oil in industrial fluids and it is known to separate out of solution readily. The reformulated custom fluids are shown in Table 5.8. Castrol 6519 and Trim E206nd, at a 5% concentration in DI water, were again used for control fluids. All fluids were subjected to five replicate holes and were run in a randomized order.

As with Custom Formulations 1 and 2, the drilling forces and temperature used to characterize lubrication and cooling functionality were determined using the drilling test methodology developed by Greeley et al. (2003). In evaluating all of the solutions, five replicate holes were drilled for each of the seven (7) formulations. All of the 35 holes were drilled in a completely randomized order. Table 5.9 shows the average and standard deviation of the machining tests.

Table 5.8. Final Custom Formulation (CF) Components.

CF	Surface Tension	EP Additive	Boundary Lubricant	Hydrodynamic Lubricant
3	72 mN/m	1%	2%	2%
4	30 mN/m	1%	2%	2%
5	72 mN/m	0.2%	0.4%	0.4%
6	30 mN/m	0.2%	0.4%	0.4%

Table 5.9. Reformulated Custom Fluid Machining Test Results.

Fluid	**Average**	**St. Deviation**
DI H2O		
Average Torque (N-cm)	1137.95	23.69
Average Thrust (N)	1198.72	13.73
Max Temp (C)	99.26	2.48
6519 (5%)		
Average Torque (N-cm)	1089.55	15.52
Average Thrust (N)	1143.18	20.72
Max Temp (C)	89.41	1.71
Trim E206nd (5%)		
Average Torque (N-cm)	1057.14	7.34
Average Thrust (N)	1120.73	19.90
Max Temp (C)	86.41	0.78
Custom Formulation 3		
Average Torque (N-cm)	1039.28	26.99
Average Thrust (N)	1079.92	32.10
Max Temp (C)	97.33	1.12
Custom Formulation 4		
Average Torque (N-cm)	1034.01	16.94
Average Thrust (N)	1087.67	16.58
Max Temp (C)	94.57	1.31
Custom Formulation 5		
Average Torque (N-cm)	1042.56	27.80
Average Thrust (N)	1100.55	20.18
Max Temp (C)	89.53	0.73
Custom Formulation 6		
Average Torque (N-cm)	1023.77	38.89
Average Thrust (N)	1076.36	44.93
Max Temp (C)	89.17	0.80

Using pair-wise, two-tailed t-tests with α = 0.05, the solutions with a 5% oil concentration were once again found to not provide adequate cooling capabilities when compared to the industrial MWF. However, this round of testing showed that the functionality of solutions with an oil content of 1% compared favorably to the industrial fluids. The two formulations that had an oil content of 1% (99% DI with UCon; 98.9% DI and 0.1% 91-6 with UCon) performed comparably, or in some cases better, than the industrial fluids in terms of both lubrication and cooling. The 1% oil content fluids were also much easier to separate. Table 5.10 summarizes the t-test results.

Table 5.10. t-Test Results for Final Machining Tests.

t-Test Between Means	Torque	Thrust	Temperature
DI versus 6519	Different	Different	Different
DI versus Trim	Different	Different	Different
DI versus Custom 3	Different	Different	Not Different
DI versus Custom 4	Different	Different	Different
DI versus Custom 5	Different	Different	Different
DI versus Custom 6	Different	Different	Different
6519 versus Trim	Different	Not Different	Different
6519 versus Custom 3	Different	Different	Different
6519 versus Custom 4	Different	Different	Different
6519 versus Custom 5	Different	Different	Not Different
6519 versus Custom 6	Different	Different	Not Different
Trim versus Custom 3	Not Different	Different	Different
Trim versus Custom 4	Different	Different	Different
Trim versus Custom 5	Not Different	Not Different	Not Different
Trim versus Custom 6	Not Different	Not Different	Not Different
Custom 3 versus Custom 4	Not Different	Not Different	Different
Custom 3 versus Custom 5	Not Different	Not Different	Different
Custom 3 versus Custom 6	Not Different	Not Different	Different
Custom 4 versus Custom 5	Not Different	Not Different	Different
Custom 4 versus Custom 6	Not Different	Not Different	Different
Custom 5 versus Custom 6	Not Different	Not Different	Not Different

5.3 Chapter Summary

1. The findings from the EP additive and boundary lubrication regimes testing indicated that a fluid with a surface tension of 30 mN/m, 5% concentration of oil, and a particle size of 5 microns or less provides the best combination of cooling and lubrication.

2. It was determined from the particle size investigation that after mixing the fluid it is important to allow the formulation to sit for 24 hours prior to remixing and application to ensure proper particle size.

3. To get all three oils to separate out of solution, it will be necessary to heat the fluid so that the inversely soluble hydrodynamic lubricant will precipitate out.

4. When the custom formulations were compared to industrial MWFs it was determined that a lower concentration of oil (0.2% EP additive, 0.4% boundary lubricant, 0.4% hydrodynamic lubricant) provided the best balance in terms of both cooling and lubrication.

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

For the research presented in this report, the stated objective was to develop a rational approach to designing transiently stable emulsions by elucidating the important factors affecting lubrication, cooling, and phase separation. To accomplish this, the research had the following two sub-objectives:

1. Understand the lubrication and cooling properties of constituents of transiently stable two-phase mixtures as metalworking fluids (MWFs).
2. Better understand the separation kinetics and phase composition of the two-phase mixtures.

Through experimental evaluation, this research characterized lubricating and cooling functionality using the metrics of drilling forces, namely torque and thrust, and drilling temperature, respectively. Separation kinetics were determined by analyzing the quantity of oil phase separation out over time. The effect of centrifugation on accelerating phase separation was also investigated. Based on machining tests, transiently stable emulsions performed as well, and in some cases better, than the industrial MWFs. The following specific conclusions can be drawn from this study.

6.1.1 <u>Effect of Water Phase Surface Tension and Viscosity on Metalworking Fluid Functionality</u>

1. Using glycol ethers, experimental investigation revealed that a lower surface tension, and thus better wettability, will indeed reduce temperatures during machining. In similar testing done with surfactants, the results showed that surfactants can also provide surface tension reducing properties that lead to better cooling functionality during machining. It was found that once the surface tension value was at or below approximately 35 mN/m, significant decreases in temperature were observed.
2. In a comparative analysis of the ether and surfactant solutions, it was found that a lower surface tension, independent of the type of chemical used to lower it, provided better cooling. Also, the glycol ether solutions seemed to provide better cooling than surfactant solutions at higher surface tensions; however, the concentration needed for the ether solutions was considerably higher than the surfactant solutions (9% versus 0.01% for 37 mN/m).
3. Separate experiments with varying viscosities showed that as the viscosity of a solution increased, the cutting forces decreased suggesting that friction between

the chip/workpiece and the tool was reduced. By increasing the viscosity of the MWF just 0.3 cP above deionized water, a significant decrease in machining forces was realized. The varying viscosities and associated low surface tensions demonstrated through reduced cutting temperatures the combined effects of these two fluid properties.

6.1.2 Effect of Particle Size and Proportion of Oil on Metalworking Fluid Functionality

1. With the EP additive being blended into smaller particles, it was able to fill interstitial gaps (between the tool and workpiece and tool and chip), which a larger particle may not have been able to penetrate, thus increasing the cooling capability of the fluid.

2. The net effect of small particle size, which reduces the heat generated, combined with a low surface tension is better overall temperature reduction.

3. At a high surface tension value, the particle size has an effect on machining performance because the solution does not contain any surfactants; therefore, the EP additive does not break down as readily into solution, or form smaller particles, and may not lubricate as well.

4. With the boundary lubricant, the lowest maximum temperature occurs when particle size is large, the proportion of oil is at its highest level, and surface tension is at its lowest level.

5. The boundary lubricants performed better in terms of friction reduction at a higher surface tension value, or without surfactants. No surfactant means that the boundary lubricant will separate out of solution more readily.

6. The lubricity capabilities of the optimal boundary lubricant formulation were comparable to an industrial formulation; however, the cooling capabilities of the boundary lubricant formulation were inferior to the industrial MWF.

6.1.3 Formulation and Investigation of Custom Two-Phase Metalworking Fluids

1. The findings from the study on surface tension and viscosity – provided by the hydrodynamic lubrication regime – were the basis for formulating the transiently stable two-phase mixture. The findings from the EP additive and boundary lubrication regimes testing indicated that a fluid with a surface tension of 30 mN/m, 5% concentration of oil, and a particle size of 5 microns or less provides the best combination of cooling and lubrication.

2. The particle size investigation of the custom formulations illuminated an additional consideration when all three regimes are used concurrently. It was determined from this investigation that after mixing the fluid it is important to allow the formulation to sit for 24 hours prior to machining to give it adequate

time for chemical reactions to take place. If this time frame is not observed, the particle size is undeterminable and not consistent. In addition, oil in excess of that required to achieve adequate lubrication is counterproductive to achieving cooling performance.

3. The presence of surfactants may interfere with achieving boundary lubrication at low boundary lubricant concentration. This implies that further care must be taken to select surfactants that are either neutral or synergistic with boundary lubricants.

4. When the custom formulations were compared to industrial MWFs, it was determined that a lower concentration of oil (0.2% EP additive, 0.4% boundary lubricant, 0.4% hydrodynamic lubricant) provided the best balance in terms of both cooling and lubrication.

6.2 Recommendations for Future Work

- The stability of the oil-water mixture was mainly studied in relation to the particle size of the emulsion. Separation kinetics were also determined by analyzing the quantity of oil phase separating out over time. The effect of centrifugation on accelerating phase separation was also investigated. However, additional emulsion stability studies on the final formulation could be conducted spectrophotometrically by measuring turbidity at multiple wavelengths as a function of time and determining the wavelength exponent (Deluhery and Rajagopalan, 2005).

- In the freshly formulated fluids studied, the stability properties of the mixture, its surface tension and particle size, were favorable; however the introduction of particulate matter over a period of time might adversely affect separation. It will therefore be important to investigate this by artificially introducing grinding fines or chips at appropriate levels to evaluate the effect they have on separation of the fluid. The purity of the oil phase could be determined by measuring the moisture content of the oil and that of the water phase by measuring the amount of fats, oils, and greases (FOG) in the water.

- The transiently stable fluid was evaluated in machining tests versus industrial MWFs based upon the drilling testbed developed by Greeley et al. (2003). However, the transiently stable fluid could be tested for a limited period of time under normal machining conditions. The testing should focus on determining tool life, effectiveness of the transiently stable mixture over time, and ease of purification. Purification should be accomplished primarily by settling, separation of the water phase, and replacing with fresh water. An industrial MWF should be used as the control fluid for the studies on tool life.

- A classification system that identifies chips based on their size and morphology could be conducted. It has been shown that using this procedure is one way to distinguish between different cutting conditions (Shih et al., 2004); therefore it follows that the chip morphology could be used to distinguish between different fluids, or even different fluid properties.

- Surface finish is an important parameter of a drilled hole. It can determine if the concentration of the MWF mixture is too low, if the MWF is not reaching the metal removal area, if the MWF is contaminated with chips or tramp oil, and if the dilution water may be too hard for the MWF concentrate. A study based upon the surface roughness of the drilled holes would be informative.

List of References

Abanto, M., J. Byers, and H. Noble. 1994. The Effect of Tramp Oil on Biocide Performance in Standard Metalworking Fluids. *Lubrication Engineering* 50: 732-737.

ASTM D5619. 2005. Standard Test Method for Comparing Metal Removal Fluids Using the Tapping Torque, *ASTM International (for referenced ASTM standards)*.

Benes, J. 2006. Maximizing Coolant Endurance and Economy. *American Machinist*, Penton Media.

Benito, J. M., G. Rios, B. Gutierrez, C. Pazos, and J. Coca. 1999. Integrated Process for the Removal of Emulsified Oils from Effluent in the Steel Industry. *Separation Science and Technology* 34(15): 3031-3043.

Bennett, E.O. 1974. Water Quality and Coolant Life. *Lubrication Engineering* 30(11): 549-555.

Bittorf, P. J., S. G. Kapoor, R. E. DeVor, and N. Rajagopalan. 2006. Effect of Water Phase Surface Tension and Viscosity on Metalworking Fluid Functionality. *Transactions of the North American Manufacturing Research Conference* 34: 555-562.

Bittorf, P. J., S. G. Kapoor, R. E. DeVor, and N. Rajagopalan. 2007. Transiently Stable emulsions for Metalworking Fluids. *Transactions of the North American Manufacturing Research Conference* 34: 555-562.

Brockhoff, T. and A. Walter. 1998. Fluid Minimization in Cutting and Grinding. *Abrasives* Oct-Nov: 38-42.

Byers, J.P., ed. 1994. *Metalworking Fluids*. New York, NY, Marcel Dekker.

Canter, N. 2005. HLB: A New System for Water-Based Metalworking Fluids. *Tribology & Lubrication Technology* 61(9): 10-12.

Cheryan, M. and N. Rajagopalan. 1998. Membrane Processing of Oily Streams. Wastewater Treatment and Waste Reduction. *J. Membrane Science* 151: 13-28.

Deluhery, J. and N. Rajagopalan. 2005. A Turbidimetric Method for the Rapid Evaluation of MWF Emulsion Stability. *Colloids and Surfaces* 256: 145-149.

Eppert, J.J. 2002. Modeling the Effects of Selective Component Depletion via Tramp Oil Extraction and Chip Adsorption in Industrial Metalworking Fluid Systems. M.S. Thesis, University of Illinois, Urbana-Champaign, Urbana, IL.

Gauthier, S. L. 2003. Metalworking Fluids: Oil Mist and Beyond. *Applied Occupational and Environmental Hygiene* 18: 818-824.

Greeley, M. H. 2002. Evaluations of Metalworking Fluid Functionality using a Novel Drilling-Based Methodology. M.S. Thesis, University of Illinois, Urbana-Champaign, Urbana, IL.

Greeley, M. H., R. E. DeVor, S. G. Kapoor, and N. Rajagopalan. 2003. Evaluating Performance Changes due to Gradual Coponent Depletion in Metalworking Fluids. *Transactions of the North American Manufacturing Research Conference* 31: 337-344.

Greeley, M. H., R. E. DeVor, S. G. Kapoor, and N. Rajagopalan. 2004. The Influence of Fluid Management Policy and Operational Changes on Metalworking Fluid Functionality. *ASME J. Manufacturing Science and Engineering* 126: 445-450.

Hetsroni, G., M. Gurevich, A. Mosyak, R. Rozenbilt, and Z. Segal. 2004. Boiling Enhancement with Environmentally Acceptable Surfactants. *Int. J. Heat and Fluid Flow* 25: 841-848.

Hunz, R. P. 1984. Water-Based Metalworking Lubricants. *Lubrication Engineering* 40: 549-553.

Khudobin, L. V. and Y. V. Polyanskov. 1982. How the Properties of Cutting Fluids Affect Metal-Cutting Processes. *Soviet Engineering Research* 53: 23-25.

Ladov, E. N. 1973. A Tapping Test for Evaluating Cutting Fluids. *Lubrication Engineering* 30(1): 5-9.

Mandakovic, R. 1999. Assessment of EP Additives for Water-Miscible Metalworking Fluids. *J. Synthetic Lubrication* 16(1): 13-26.

Mahdi, S. M. and R. O. Skold. 1990. Surface Chemistry Aspects on the Use of Ultrafiltration for the Recycling of Waterbased Synthetic Metalworking Fluids: Component Studies. *J. Dispersion Science Technology* 11: 1-30.

Marano, R. S., G. S. Cole, and K. R. Carudner. 1991. Particulate in Cutting Fluids: Analysis and Implications in Machining Performance. *Lubrication Engineering* 47: 376-382.

Master Chemicals Corporation. *Trim Coolants and Metalworking Fluids*. 1998. http://www.masterchemical.com (Accessed March 31, 2006).

Merchant, M. E. 1950. Fundamentals of Cutting Fluid Action. *Lubrication Engineering* 6: 163-167.

Misra, S. K. and R. O. Skold. 1999. Membrane Filtration Studies of Inversely Soluble Model Metalworking Fluids. *Separation Science and Technology* 34: 53-67.

Nachtman, E. S. and S. Kalpakjian. 1985. *Lubricants and Lubrication in Metalworking Operations*. New York, NY, Marcel Dekker.

Polyanskov, et al. 1986. Improved Preparation of Water-Based Fluids. *Soviet Engineering Research* 6(2): 73-74.

Quingwen, Q., W. Mei, W. Lihua, and C. Shan. 2002. A Continuous Viscosity Model for Thin Film Lubrication. *Tribology International* 35: 459-465.

Rajagopalan, N., T. Rusk, and M. Dianovsky. 2004. Purification of Semi-Synthetic Metalworking Fluids by Microfiltration. *Tribology and Lubrication Technology* 60(8): 38-44.

Rinkus, K. M., W. Lin, A. Jha, and B. E. Reed. 1997. Investigation into the Nature and Extent of Microbial Contamination. Proceedings of the *52nd Purdue Industrial Waste Conferences*, 601-610.

Rios, G., C. Pazos, and J. Coca. 1997. Destabilization of Cutting Oil Emulsion Using Inorganic Salts as Coagulants. *Colloids and Surfaces* 138: 383-389.

Rios, G., C. Pazos, and J. Coca. 1998. Zeta Potentials of Cutting Oil-Water Emulsions: Influences of Inorganic Salts. *J. Dispersion Science and Technology* 19(5): 661-678.

Serra-Holm, V. 2002. Naphthenic Oil Best for Metalworking. *Naphthenics Market Magazine*.

Shih, A. J., J. Luo, M. A. Lewis, and J. S. Strenkowski. 2004. Chip Morphology and Forces in End Milling of Elastomers. *ASME J. Manufacturing Science and Engineering* 126: 124-130.

Silliman, J. D. 1992. *Cutting and Grinding Fluids: Selection and Application*, 2nd edition. Dearborn, MI, Society of Manufacturing Engineers.

Skerlos, S. J., N. Rajagopalan, R. E. DeVor, S. G. Kapoor, and V. D. Angspatt. 2000a. Ingredient-Wise Study of Flux Characteristics in the Ceramic Membrane Filtration of Uncontaminated Synthetic Metalworking Fluids, Part 1: Experimental Investigation of Flux Decline. *ASME J. Manufacturing Science and Engineering* 122(4): 739-745.

Skerlos, S. J., N. Rajagopalan, R. E. DeVor, S. G. Kapoor, and V. D. Angspatt. 2000b. Ingredient-Wise Study of Flux Characteristics in the Ceramic Membrane Filtration of Uncontaminated Synthetic Metalworking Fluids, Part 2: Analysis of Underlying Mechanisms. *ASME J. Manufacturing Science and Engineering* 122(4): 746-752.

Skerlos, S. J., N. Rajagopalan, R. E. DeVor, S. G. Kapoor, and V. D. Angspatt. 2001. Microfiltration of Polyoxyalkylene Metalworking Fluid Lubricant Additives Using Aluminum Oxide Memebranes. *ASME J. Manufacturing Science and Engineering* 123: 692-699.

Skold, R. O. and M. A. R. Tunius. 1994. Adsorption of Bis(triethylammonium) 1.10-Decanedicarboxylate on Magnetite from Aqueous Solution. *Langmuir* 10: 211-217.

Srijaroonrat, P., E. Julien, and Y. Aurelle. 1999. Unstable Secondary Oil/Water Emulsion Treatment using Ultrafiltration: Fouling Control by Backflushing. *Journal of Membrane Science* 159: 11-20.

van Antwerpen, F. 2000. Removal Fluids on the Move in Coolants/Lubricants for Metal Cutting & Grinding: *Technology & Market Outlook 2000*, Chicago, IL, June 5-7, 2000. Gorham, Maine, Gorham Advanced Materials, Inc.

Van der Bruggen, B., C. Vandecasteele, T. Van Gestel, W. Doyen, and R. Leysen. 2003. A Review of Pressure-Driven Membrane Processes in Wastewater Treatment and Drinking Water Production. *Environmental Progress* 22(1): 46-56.

Wen, D. K., and B. X. Wang. 2002. Effects of Surface Wettability on Nucleate Pool Boiling Heat Transfer for Surfactant Solutions. *Int. J. Heat and Mass Transfer* 45: 1739-1747.

Yan, S. and S. Kuroda. 1997. Lubrication with Emulsion II. The Viscosity Coefficients of Emulsions. *Wear* 206: 238-243.

Zimmerman, J. B., K. F. Hayes, and S .J. Skerlos. 2004. Influence of Ion Accumulation on the Emulsion Stability and Performance of Semi-Synthetic Metalworking Fluids. *Environmental Science and Technology* 38(8): 2482-2490.