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EXPERIMENTAL COMPARISON OF VEGETABLE AND PETROLEUM BASE OILS IN METALWORKING FLUIDS USING THE TAPPING TORQUE TEST

Andres F. Clarens[1] **Julie B. Zimmerman**[2] **Heather R. Landis**[3] **Kim F. Hayes**[1] **Steven J. Skerlos**[3]

1. Department of Civil and Environmental Engineering
3. Department of Mechanical Engineering
The University of Michigan at Ann Arbor

2. Office of Research and Development
Environmental Protection Agency

ABSTRACT

Traditional metalworking fluid (MWF) formulations have been associated with a number of environmental and health concerns that have driven recent efforts to develop new formulations based on alternative vegetable and ester based feed stocks. This study uses the tapping torque test to compare the performance of five base oil feedstocks for MWFs: naphthenic mineral oil, a 50/50 blend of naphthenic and paraffinic mineral oil, soybean oil, canola oil (75% oleic content), and a TMP Ester. The five oils were tested as straight oils, and as soluble oil and semi-synthetic MWFs, to understand the impacts of emulsification on base oil performance. Machining performance was evaluated using a modification to the standard tapping torque test (ASTM D 5619) previously established by the authors. Over 500 tapping torque experiments are represented in this research. The results indicate that as straight oils all vegetable based stocks perform significantly better than the mineral oils. This trend holds, although is much less pronounced, after the vegetable stocks are emulsified into soluble oil and semi-synthetic MWFs. The results also indicate that some vegetable oil base stocks have a higher potential for lubricity than others, with data revealing that the soy and TMP ester provide improved tapping torque efficiency relative to canola oil in emulsified MWFs.

KEY WORDS

Metalworking fluids, vegetable base oils, EP additives, particle size, tapping torque test

INTRODUCTION

Sustainable aqueous systems minimize life cycle environmental impact by 1) minimizing the materials, energy, and toxicity of system inputs and outputs, and 2) achieving maximum system lifespan by maintaining physical, biological, and chemical parameters within limits appropriate to system function. Although it is estimated that over 1 billion gallons of *metalworking fluids* (MWFs) are consumed each year, metalworking fluid systems are universally in violation of these principles, and the need to develop basic knowledge and technology to achieve sustainability has been increasingly recognized in recent years.

By serving as both coolants and lubricants, metalworking fluids (MWFs) are critical to a wide range of manufacturing operations [1]. However, MWFs are harmful to the environment due to their high oil content, biochemical oxygen demand, surfactants, and because they serve as carriers for hazardous metals and chemicals [2]. Moreover, the U.S. EPA has proposed regulations that would limit the discharge of oil and grease to 35 mg/l [3]. This is significant because MWFs can contain over 6,000 mg/l of these constituents, and meeting the standard would require large investments in end-of-pipe treatment technologies. Despite these environmental and health risks, and high disposal costs, MWF use remains strong and continues to grow [4].

Mitigation of these financial, environmental, health, and performance liabilities requires innovative eco-design of MWF formulations toward the development of *sustainable metalworking fluid systems* (Figure 1). This includes a re-evaluation of the chemical constituents found in MWFs. The principal components of the most common MWFs used today (i.e., soluble oils and semi-synthetics) are petroleum-based mineral oil for lubrication emulsified in water for cooling. Recently, there has been increasing interest in developing "green" MWFs derived from renewable bio-based oils and more environmentally benign additives [5]. Numerous bio-based oils are available on the market, and the authors have shown in [6] for the case of canola oil-based MWFs that such vegetable oil feedstocks are likely to represent an environmentally preferable alternative to mineral oil. This is true particularly when greenhouse gas emissions are considered

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采用攻丝扭矩试验对金属加工液中植物基油与石油基油进行实验对比

安德烈斯·F·克莱伦斯[1]朱莉·B·齐默尔曼[2]海瑟·R·兰迪斯[3]金·F·海斯[1]史蒂文·J·斯克洛斯[3]

1. 土木与环境工程系

3. 机械工程系密歇根大学安娜堡分校

2. 环境保护局研究与发展办公室

摘要

传统金属加工液（MWF）配方长期存在诸多环境与健康隐患，这促使业界近期致力于开发基于替代性植物油及酯类原料的新配方。本研究采用扭力测试法对比了五种基础油原料在金属加工液中的性能表现：环烷基矿物油、环烷基与链烷基矿物油50/50混合油、大豆油、菜籽油（含油酸75%）以及 TMP 酯。通过将五种基础油分别作为纯油、可溶性油及半合成金属加工液进行测试，以探究乳化作用对基础油性能的影响。加工性能评估采用作者改良版标准扭力测试法（ASTM D 5619），本研究共完成500余组扭力实验数据。结果表明：纯油状态下，所有植物基原料均显著优于矿物油；当植物基原料被乳化为可溶性油或半合成金属加工液后，该优势趋势虽有所减弱但仍持续存在。研究结果还表明，某些植物油基础油品的润滑潜力高于其他品种。数据显示，在乳化微乳化燃料油体系中，大豆油和 TMP 酯相较于菜籽油能提供更高的抽吸扭矩效率。

关键词

金属加工液、植物基油、EP添加剂、粒径、攻丝扭矩测试

引言

*可持续水系统*通过两大核心机制实现生命周期环境影响最小化：其一，最大限度减少系统输入与输出环节中的材料消耗、能源使用及毒性物质；其二，通过将物理、生物及化学参数维持在适配系统功能的合理范围内，从而确保系统使用寿命最大化。尽管据估算全球每年消耗的*金属加工液*（MWFs）超过10亿加仑，但金属加工液系统普遍违背这些可持续性原则。近年来，业界日益认识到亟需通过积累基础理论知识与开发关键技术来实现系统可持续发展。

金属加工液（MWFs）兼具冷却剂和润滑剂双重功能，对各类制造工艺至关重要[1]。然而，由于其高含油量、生化需氧量、表面活性剂特性，以及作为有害金属和化学品载体的作用[2]，MWFs对环境具有危害性。此外，美国环保署（EPA）已提出法规，将油类和油脂排放限值设定为35 mg/l[3]。这一标准具有重要意义，因为MWFs中这些成分的含量可超过6,000 mg/l，达到标准需对末端处理技术进行巨额投资。尽管存在这些环境与健康风险及高昂处置成本， MWF 使用仍保持强劲势头并持续增长[4]。

要缓解这些财务、环境、健康及性能方面的责任，需要通过创新生态设计来优化 MWF 配方，以开发*可持续金属加工液系统*（图1）。这包括对金属加工液中化学成分的重新评估。当前最常用的金属加工液（即可溶性油和半合成油）主要由石油基矿物油作为润滑剂与水乳化形成冷却液。近年来，开发源自可再生生物基油及更环保添加剂的“绿色”金属加工液日益受到关注[5]。市场上已有多种生物基油可供选择，作者在[6]针对菜籽油基金属加工液的研究表明，这类植物油原料很可能成为矿物油更环保的替代品。尤其在考虑温室气体排放因素时，这一优势更为显著。

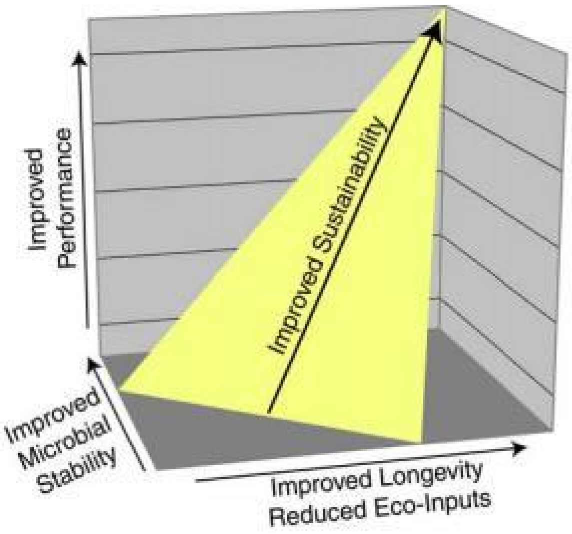

Figure 1. Target objectives for sustainable MWF systems

because carbon dioxide is sequestered when the vegetable feedstocks are grown. Problematic characteristics of MWFs, such as odors and degradation caused by biological growth, cannot be predicted nor evaluated prior to formulation, although preliminary studies suggest that bio-based fluids do not possess inherent disadvantages in these areas relative to petroleum based MWFs [5]. For instance, the vegetable based emulsifier systems currently being considered for MWFs tend to be more hard water stable, and biological stability has been shown to correlate closely with particle size [10], dispelling the popular sentiment that bio-based fluids are inherently more susceptible to microbial attack. Moreover, vegetable based MWFs might hold other advantages in manufacturing environments. For instance, they may be less likely to produce harmful process by-products such as aromatic hydrocarbon aerosols.

While interest in bio-based oils as feedstocks for MWFs is increasing, little information is available in the literature regarding their performance as MWFs relative to conventional alternatives. Therefore this paper compares the relative performance of five base oils in straight and emulsified form for their performance in the tapping torque test. Specifically, three common bio-based oils available on the market (canola, soy, and a synthetic ester) were tested and compared to two common mineral oils used in lubricants (a naphthenic and a 50/50 naphthenic/paraffinic blend). The performance of these base stocks is evaluated in tapping operations involving both 1018 and 4140 steel workpieces. Results describing the significance of the tapping torque efficiency metric in terms of its correlation with known field performance are also provided, along with a discussion regarding the potential roles of emulsion particle size and extreme pressure (EP) additives in modifying the observed tapping torque trends for petroleum and vegetable base oils.

EXPERIMENTAL MATERIALS AND METHODS

Formulations. The MWF formulations considered here were based on a generic formula provided by a commercial MWF supplier. The MWFs were first produced in concentrated form, and then were diluted to a working concentration in deionized water. This formulation procedure is consistent with the manner in which MWFs are prepared and utilized in practice. All MWF concentrates consisted of 1.5 wt% coupler (butyl carbitol), 3.7 wt% tall oil fatty acid, 7.9 wt% corrosion inhibitor (monoethanol anime), 15 wt% oil, and 14 wt% surfactants, and 57 wt% deionized water. For comparative purposes, the MWFs investigated differed only in base oil and surfactant system chemistry. The surfactant system chosen for each base oil is listed in Table 1 (as concentrate). Three basic MWFs were developed for each base oil, a straight oil (with no deionized water, surfactants, or other MWF additives), a soluble oil (concentrate diluted 77% in deionized water), and a semi-synthetic (concentrate diluted 95% in deionized water). As tested, the MWFs either contained 100% oil (straight oil), 3.4% oil (soluble oil), or 0.75% oil (semi-synthetic). Within a class of MWF, (straight oil, soluble oil, or semi-synthetic) the oil concentrations were always held equal to permit comparison of the base oil functionality. It was found for these MWFs that the additives listed above (other than oils and surfactants) had little impact on emulsification, performance, and stability.

Materials. For the five different base MWF formulations, all of the fluid components were used as delivered from the manufacturer and were subject to the same handling and storage conditions.

Oil type	*Oil % weight in concentrate*	*primary surfactant type*	*primary surfactant % weight in concentrate*	*secondary surfactant type*	*secondary surfactant % weight in concentrate*
Naphthenic	90	Tagat V 20	4.5	Alfonic 1216 CO-1.5 Ethoxylate	5.5
50/50 Blend	90	Tagat V 20	4.5	Alfonic 1216 CO-1.5 Ethoxylate	5.5
Canola Oil	83	Tagat V 20	12.75	Tegin OV	4.25
Soybean Oil	83	Tagat V 15	12.25	Tegin OV	4.75
TMP Ester	90	Tagat V 20	10	none	none

Table 1. Oils and Surfactants used to make MWF Emulsions

The base oils used in the formulations were a petroleum-based naphthenic oil, a petroleum-based 50/50 naphthenic/paraffinic oil blend, a bio-based high oleic canola oil that was modified for oxidative stability (Agri-Pure 75, Cargill Inc., Minneapolis, Minnesota), a bio-based soybean oil (Alkali Refined Soybean Oil, Cargill Inc., Minneapolis, Minnesota), and a bio-based synthetic TMP ester (Priolube 1427 Trimethylolpropane triolate, Uniqema, New Castle, Delaware). Combinations of four different surfactants were used to make stable emulsions ofthe oils. The surfactants were Tagat V20, Tagat V15 and Tegin OV (Degussa-Goldschmidt Chemical Corporation, Hopewell, Virginia) and Alfonic 1216 CO-1.5 Ethoxylate (Sasol North America, Austin Texas). While it would have been preferable for comparisons to use identical surfactant systems for each base oil, it was verified that it is not possible to utilize a single surfactant system for the emulsification of these different base oils. This is a deep rooted and well known conclusion often encountered in the emulsion science literature, which considers the functionality of

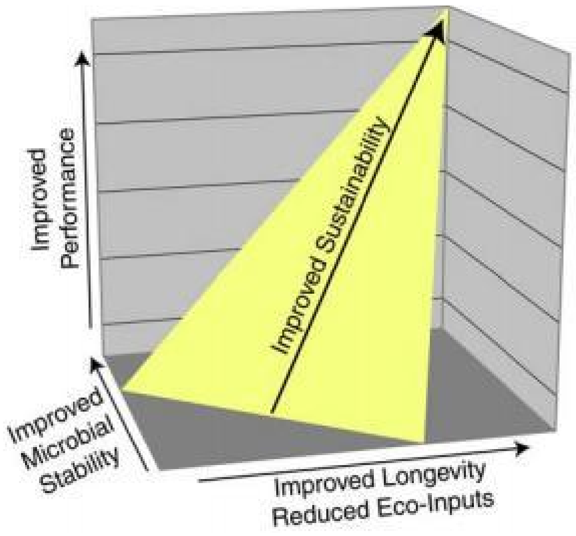

图1. 可持续 MWF 系统的目标指标

由于植物原料在种植过程中会固存二氧化碳，因此微生物废水（MWFs）在配制前无法预测或评估其异味问题及生物生长导致的降解特性 。尽管初步研究表明，与石油基MWFs相比 ，生物基液体在这些方面并不具备固有缺陷[5] 。例如，当前用于MWFs的植物基乳化剂体系通常具有更强的硬水稳定性，且研究证实生物稳定性与颗粒尺寸密切相关[10] ，这打破了 “生物基液体天生更易受微生物侵蚀” 的普遍认知。此外，植物基MWFs在生产环境中可能具备其他优势：例如更不易产生芳香烃气溶胶等有害工艺副产物。

尽管生物基油作为矿物基润滑油（MWFs）原料的市场需求持续增长，但现有文献中关于其相对于传统替代品的润滑性能数据仍较为匮乏。为此，本研究通过切削扭矩测试，系统比较了五种基础油在直链形态与乳化形态下的相对性能表现 。实验选取市场上三种常见生物基油（菜籽油、大豆油及合成酯油）与两种基础润滑油中常用的矿物油（环烷基油及50/50环烷基/链烷基混合油）进行对比测试。通过1018钢与4140钢工件切削作业评估基础油性能表现，并结合扭矩效率指标与实际现场数据的相关性分析，揭示该指标的理论意义。研究还探讨了乳化液粒径及极压添加剂对石油基油与植物基油切削扭矩变化趋势的潜在调控作用。

实验材料与方法

配方 。本文研究的 MWF 配方均基于商业 MWF 供应商提供的通用配方。MWFs首先以浓缩形式制备，随后用去离子水稀释至工作浓度。该配方制备工艺与实际应用中MWFs的制备及使用方式一致。所有 MWF 浓缩液均包含1.5 wt%偶联剂（丁基卡比醇）、3.7 wt%松香脂肪酸、7.9 wt%缓蚀剂（单乙醇胺）、15 wt%油相、14 wt%表面活性剂及57 wt%去离子水。为便于对比，所研究的MWFs仅在基础油与表面活性剂体系化学成分上存在差异。各基础油所选表面活性剂体系列于表1（浓缩液形式）。针对每种基础油开发了三种基础MWFs：直链油（不含去离子水、表面活性剂或其他 MWF 添加剂）、可溶性油（浓缩液用去离子水稀释77%）及半合成油（浓缩液用去离子水稀释95%）。测试结果显示，MWFs油相含量分别为100%（直链油 ）、3.4%（可溶性油 ） 或0.75%（半合成油 ）。在MWF 类别（直链油、可溶性油或半合成油） 中，始终将油浓度保持一致， 以便比较基础油的功能性。研究发现，对于这些微乳液分散体（MWFs），上述添加剂（除油类和表面活性剂外）对乳化性能、使用效果及稳定性影响甚微。

材料 。针对五种不同基础 MWF 配方，所有流体组分均采用制造商原厂提供的产品，并在相同操作与储存条件下使用。

油型	油 重量百分比 全神贯注	首要的 表面活性剂 类型	首要的 表面活性剂 重量百分比 全神贯注	次要的 表面活性剂 类型	次要的 表面活性剂 重量百分比 全神贯注
环烷烃类	90	Tagat V 20	4.5	Alfonic 1216 CO-1.5 乙氧基化物	5.5
50/50混合物	90	Tagat V 20	4.5	Alfonic 1216 CO-1.5 乙氧基化物	5.5
菜籽油	83	Tagat V 20	12.75	我做了卵巢切除术	4.25
大豆油	83	Tagat V 15	12.25	我做了卵巢切除术	4.75
TMP 酯	90	Tagat V 20	10	没有一个	没有一个

表1. 制备 MWF 乳剂所用油类及表面活性剂

配方中使用的基础油包括：石油基环烷油、石油基50/50环烷油/石蜡油混合油、经氧化稳定性改良的生物基高油酸菜籽油（Agri-Pure 75，嘉吉公司，明尼苏达州明尼阿波利斯市）、生物基大豆油（碱精炼大豆油，嘉吉公司，明尼苏达州明尼阿波利斯市） 以及生物基合成 TMP 酯（Priolube 1427三羟甲基丙烷三醇酯，Uniqema公司，特拉华州新堡市）。为制备油类稳定乳液，采用了四种不同表面活性剂的组合配方，具体包括：Tagat V20 、Tagat V15 、Tegin OV（德固赛-戈德施密特化学公司，弗吉尼亚州霍普韦尔市）以及Alfonic 1216 CO-1.5乙氧基化物（萨索尔北美公司，德克萨斯州奥斯汀市）。尽管理想情况下应为每种基础油选用相同表面活性剂体系进行对比研究，但经验证无法采用单一表面活性剂体系实现这些不同基础油的乳化。这一结论在乳化科学文献中具有深远影响且广为人知，其核心在于对表面活性剂功能特性的考量。

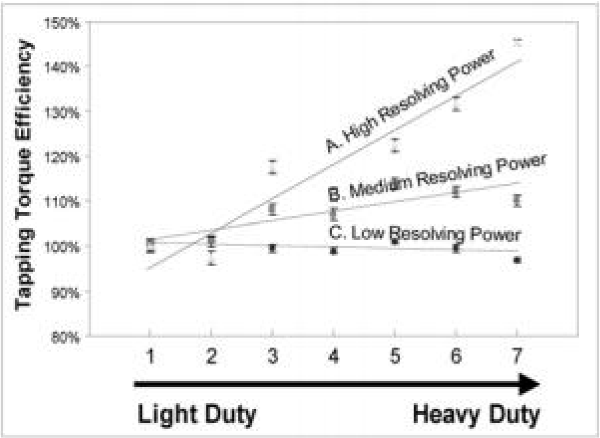

Figure 2. Non-normalized tapping torque values for 7 cutting fluids ranked from light duty to heavy duty by major supplier of MWF. (A) High resolving power condition. (B) Medium resolving power condition. (C) Low resolving power condition. After Zimmerman et al., 2003 [9]

surfactants in the stabilization of one immiscible material as a suspension in another.

The base oil formulations were made by holding the molar concentration of oil constant across all fluids. The concentrations of mineral oil in the generic recipes were used as the reference amounts of oil in the formulations. A commercially available soluble oil MWF (C225, Chrysan Industries, Plymouth, MI), was used as a benchmark to compare the oils and MWFs in the tapping experiments. C225 was utilized as it has served as a reference standard for the authors over a period of three years. The formulation for C225 was not included in Table 1 to maintain confidentiality for the manufacturer.

Methods. Emulsions were considered stable if they maintained a consistent oil-in-water particle size over a one week time period. Particle size was evaluated using photon correlation spectroscopy (PCS), which allows for the detection of subtle fluid particle size changes, including indications of coalescence. For this research, a Nicomp 370/DLS (Particle Sizing Systems, Santa Barbara, California) particle sizing system was used, with its particle size estimation capability verified independently by a wide-angle laser light scattering apparatus similar to the one described by Lee et al. [7]. Two aliquots from each formulation were analyzed by PCS and averaged.

The machining performance of the MWFs developed during this research was measured via the tapping torque test using a MicroTap Mega G8 (Rochester Hills, MI) machine tool at a machining speed of 1000 RPM on 1018 and 4140 steel workpieces that were pre-drilled and pre-reamed with 240 M6 holes (Maras Tool, Schaumburg, IL). Tapping was performed using uncoated high-speed steel taps (for 1018 steel) and CrN coated HSS taps (for 4140 steel), both with 60° pitch and 3 straight flutes. MWF evaluations were carried out according to ASTM D 5619, the Standard for Comparing Metal Removal Fluids Using the Tapping Torque Test Machine [8] with several modifications made to account for the use of a MWF evaluation testbed that permits multiple evaluations on a single workpiece as proposed by Zimmerman et al. [9]. MWF performance is reported here as percentage tapping torque efficiency (η), which is an average torque measured during tool engagement normalized to the average torque measured for a reference MWF. Higher efficiency indicates improved performance in the tapping torque test, and has been shown to be an adequate metric for field performance as discussed below. Method details are provided in [9].

Methods: Correlation of Tapping Torque Test with Field Performance [6]. As described in [9], ASTM D 5619 was designed for tapping torque test (T^3) systems that conduct a single tapping evaluation (SES) per workpiece. As might be expected, performing each test evaluation on a new workpiece introduces significant uncertainty into the evaluation process since workpiece to workpiece variation can overshadow differences in torque responses caused by MWFs. Difficulties with workpiece variation and per-test cost have led to the development of tapping torque testbeds that allow multiple test conditions to be evaluated on a single workpiece (MES). While this makes T^3 potentially more convenient and cost effective by reducing variability associated with workpiece material, this type of system introduces new challenges in experimental design and interpretation given the potential for tool wear and localized hardness within a single workpiece.

Challenges with MES, and experimental design considerations to overcome them are described in [9]. The research indicated that depending on how the tapping torque test is performed, operating conditions can either mask MWF performance (low resolving power) or provide the means to differentiate between MWF types (high resolving power). If T^3 experimental conditions with low resolving power are selected, it may be impossible to differentiate MWFs, even where known differences exist. To illustrate this, seven MWFs varying from light duty to heavy duty were examined using MES T^3. The MWF duty ratings were based upon the extensive field experience of a major MWF formulator working in a range of end-users. For T^3 experiments performed with M6 TiN tools at 1000 RPM (a condition found to have low resolving power), it was found that even the MWF with the lowest duty rating could not be statistically distinguished from the MWF with the highest duty rating (Figure 2C). However when conditions were chosen with a higher resolving power (e.g., M4, HSS tools, 1000 RPM), fluid differences were easily distinguishable and the T^3 responses were better correlated with the expected trend of MWF field performance (Figure 2B). At the test condition with the highest resolving power (M6, HSS, 1000 RPM), the expected field performance was captured even more clearly (Figure 2A). Based on Figure 2 different base oils are compared below via T^3 under high resolving power conditions.

RESULTS AND DISCUSSION

Results: Impact of Base Oil and Emulsification on T^3

Figure 3 presents the tapping torque efficiency for the five straight oils. The fluids were tested on 1018 cold rolled steel using an uncoated hardened steel tool. Under the tapping torque conditions of Figure 2A, the bio-based straight oils demonstrated significantly higher tapping torque efficiency relative to the petroleum oils. Both mineral oils had a slightly lower efficiency level relative to the reference (petroleum based, C225) soluble oil (efficiency < 100%). In contrast, the three bio-based oils exhibited a 12-14% increase in efficiency relative to the reference soluble oil.

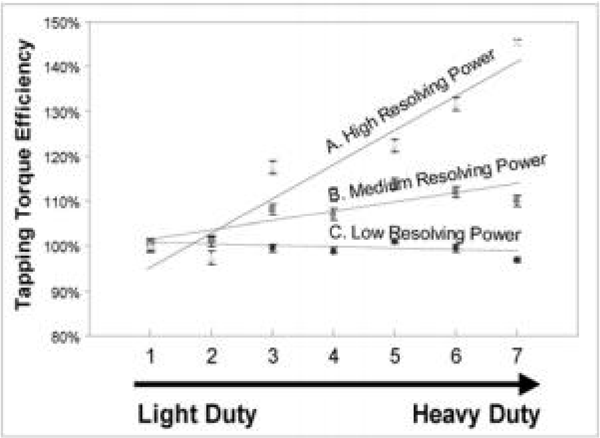

图2.按主要 MWF 供应商从轻载到重载排序的7种切削液未标准化切削扭矩值。(A)高分辨率工况。(B)中分辨率工况。(C)低分辨率工况。数据引自Zimmerman等，2003[9]

表面活性剂在稳定一种不混溶材料作为另一种悬浮液中的作用。

基础油配方的制备过程中，所有流体中的油摩尔浓度均保持恒定。通用配方中的矿物油浓度被用作配方中油含量的参考值。在抽油实验中，采用市售可溶性油 MWF（C 225，Chrysan Industries公司，美国密歇根州普利茅斯市）作为基准物质，用于对比不同油品与矿物水基燃料（MWFs）的性能。选择C225作为参照标准，是因为该产品已作为作者团队三年来的参考标准。为保护制造商商业机密，表1中未包含C225的具体配方数据。

方法。若乳剂在一周时间内能保持稳定的水包油颗粒尺寸，则判定其具有稳定性。颗粒尺寸评估采用光子相关光谱法（PCS），该技术可检测流体颗粒尺寸的细微变化，包括聚结迹象。本研究使用Nicomp 370/DLS粒度分析系统（Particle Sizing Systems公司，美国加州圣巴巴拉），其粒径估算能力已通过与Lee等人所述设备相似的广角激光光散射装置进行独立验证[7]。每种制剂各取两份样本进行PCS分析并取平均值。

本研究开发的MWFs的加工性能通过使用MicroTap Mega G8（美国密歇根州罗切斯特山）机床进行的攻丝扭矩测试进行测量，加工速度为1000 RPM，加工工件为预先钻孔并预攻丝240 M6孔（美国伊利诺伊州绍姆堡Maras Tool公司）的1018钢和4140钢。攻丝采用未涂层高速钢丝锥（用于1018钢）和CrN涂层高速钢丝锥（用于4140钢），两者均具有60 °螺距和3条直槽。MWF 性能评估依据ASTM D 5619标准进行，该标准为使用攻丝扭矩测试机比较金属去除液的标准[8]，并根据Zimmerman等人提出的允许在单个工作件上进行多次评估的 MWF 评估试验台方案进行了若干修改[9]。 MWF 性能以百分比攻丝扭矩效率形式报告。η），这是在工具接合过程中测得的平均扭矩，并以参考 MWF 测得的平均扭矩为基准进行归一化处理。更高的效率表明在攻丝扭矩测试中性能更优，且如后文所述，已被证实是评估现场性能的充分指标。具体方法详见[9]。

方法：扭转力矩测试与现场性能的相关性[6]。如[9]所述，ASTM D 5619是为扭转力矩测试（T^3）系统设计的，该系统对每个工件进行单次扭转评估（SES）。正如预期的那样，由于工件间差异可能掩盖由多因素振动引起的扭矩响应差异，对每个新工件进行测试评估会引入显著的不确定性。工件差异性与单次测试成本的难题促使开发了允许在单个工件上评估多种测试条件的扭转力矩测试台（MES）。虽然这通过降低工件材料相关变异性使T^3更具便利性和成本效益，但此类系统在实验设计和结果解读方面面临新挑战，因为单个工件内可能存在刀具磨损和局部硬度差异。

MES面临的挑战以及克服这些挑战的实验设计考虑因素在[9]中有所描述。研究表明，根据开槽扭矩测试的实施方式，运行条件要么会掩盖 MWF 性能（低分辨率能力），要么能提供区分 MWF 类型的方法（高分辨率能力）。若选择分辨率能力较低的T^3实验条件，即使存在已知差异也可能无法区分MWFs。为说明这一点，使用MES T^3对从轻载到重载的七种MWFs进行了检测。 MWF 额定值基于某大型 MWF 配方师在各类终端用户中积累的丰富现场经验。在使用M6氮化钛工具以1000 RPM进行T^3实验时（该工况被发现具有低分辨率能力），研究发现即使额定值最低的 MWF 也无法与额定值最高的 MWF 进行统计学区分（图2C）。然而当选择具有更高分辨率能力的工况时（例如在M4、HSS工具（1000转/分钟）条件下，流体差异易于区分，且T^3响应与 MWF 场性能的预期趋势相关性更强（图2B）。在分辨率最高的测试条件（M6、HSS，1000转/分钟）下，预期场性能被更清晰地捕捉（图2A）。基于图2，以下通过高分辨率条件下的T^3对不同基础油进行对比分析。

结果与讨论

结果：基础油与乳化作用对T^3的影响

图3展示了五种直链油的攻丝扭矩效率。实验采用未涂层硬化钢工具，在1018冷轧钢基材上对流体进行测试。在图2A所示攻丝扭矩工况下，生物基直链油展现出显著高于石油基油的攻丝扭矩效率。两种矿物油的效率水平均略低于参照物（石油基C225可溶性油，效率<100%）。相比之下，三种生物基油的效率较参照可溶性油提升了12%-14%。

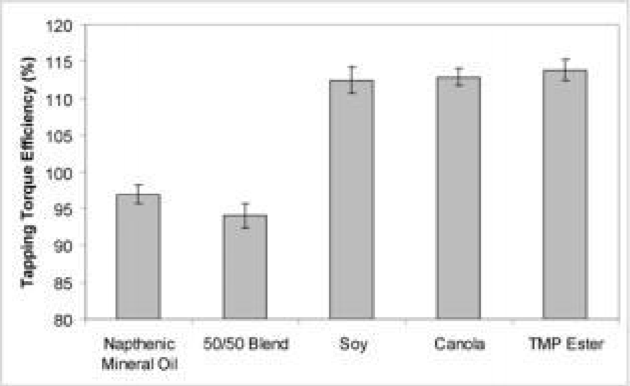

Figure 3. Tapping torque efficiency for five different base oils (napthenic mineral, napthenic/paraffinic blend, canola, soybean, and TMP ester) as straight oils (100% wt).

For the soluble oil (3.4 oil % wt) and semi-synthetic (0.75 oil % wt) formulations of these base oils, the difference in tapping torque efficiency between the petroleum and vegetable oils was found to be reduced significantly. The vegetable oils, however, still presented a significantly higher tapping torque efficiency when compared with the mineral oil based MWFs. Interestingly, the mineral oil semi-synthetic MWFs performed almost equally as well as the soluble oil MWFs in spite of the much lower oil concentration in the formulation. Figure 4 presents the tapping torque efficiency for the five oils as soluble oil and semi-synthetic emulsions. It is seen that the basic trends relative to Figure 3 are unchanged.

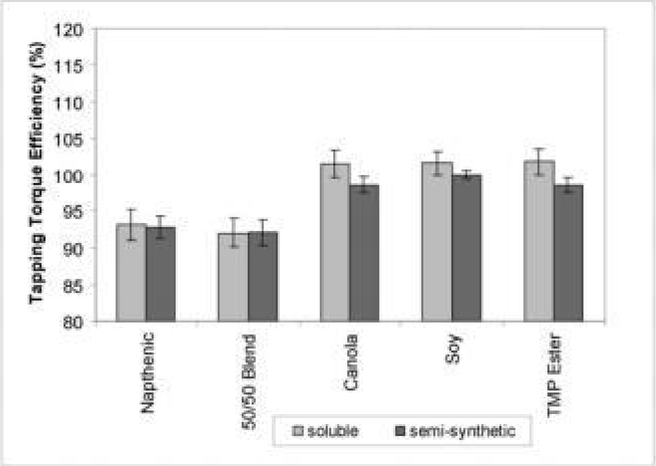

Figure 4. Tapping torque efficiency for five different base oils (napthenic mineral, napthenic/paraffinic blend, canola, soybean, and TMP ester) as soluble oil (3.4% wt), and semi-synthetic (0.75% wt) emulsions.

In order to verify these trends in the cutting of harder steels, and in the use of alternative tools (CrN coated steel), three soluble oils (based on soybean oil, mineral oil, and TMP ester) were tested via T^3 on a 4140 steel workpiece (Figure 5.). It is observed in Figure 5 that similar results were obtained when tapping 4140 steel as compared with results obtained when tapping 1018 steel (Figure 4). Once again, the fluids based on bio-feedstocks exhibited a higher tapping torque performance relative to the mineral oil based fluids. However, consistent with the trends presented in Figure 2, the differences in tapping torque efficiency are reduced, as expected given that the resolution of coated tools has been observed to be generally less than uncoated tools [9].

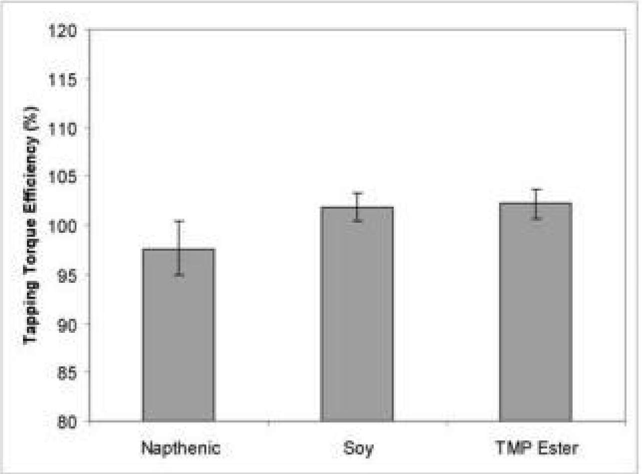

Figure 5. Tapping torque efficiency for three different base oils (napthenic mineral, soybean, and TMP ester) as soluble oil (3.4% wt) on a 4140 steel workpiece.

Results: Impact of Secondary Additives on Lubricity

Figures 3-5 provide a comparison between the base oils (including their emulsifying nonionic surfactant and anionic surfactant) as listed in Table 1 with respect to their tapping torque efficiency. In addition, experimentation was performed in this research to understand if secondary MWF ingredients (other than so-called “extreme pressure” EP additives) might play a major role in affecting the tapping torque efficiencies observed for the base oil-in-water emulsions. In general, MWFs contain a large number of secondary ingredients that may include couplers (used to clarify the appearance of the MWF), corrosion inhibitors, chelating agents (to counteract the destabilizing impact of hard water ions), pH buffers, and others.

As formulated with secondary ingredients, a semi-synthetic MWF that has been investigated extensively in previous research has the following composition [5]: 57 wt% deionized water, 1.5 wt% coupler (butyl carbitol), 3.7 wt% tall oil fatty acid, 7.9 wt% corrosion inhibitor (monoethanol anime), 15 wt% oil, 14 wt% surfactants. As shown in Figure 6, it does not appear that the presence of these secondary ingredients has a significant impact on the tapping torque efficiency for the naphthenic based MWF base emulsion. As similar results have been observed by the authors for other MWFs, this suggests that the results in Figures 3-5 are general for the base fluids they represent. This, however, does not include the possible impact on tapping torque efficiency created by the presence of EP additives which were not investigated experimentally in this research. The potential role of EP additives in innovative MWF formulations is discussed in the next section.

Discussion: Impact of EP Additives on T^3

Extreme Pressure (EP) lubrication is a version of solid-film lubrication common to MWFs in which a solid-film forms through the corrosive action of EP additives under the extreme pressure and temperature conditions of cutting processes. As illustrated in Figure 7, EP additives used in MWFs are water insoluble organic chemicals (usually organo- phosphorus,

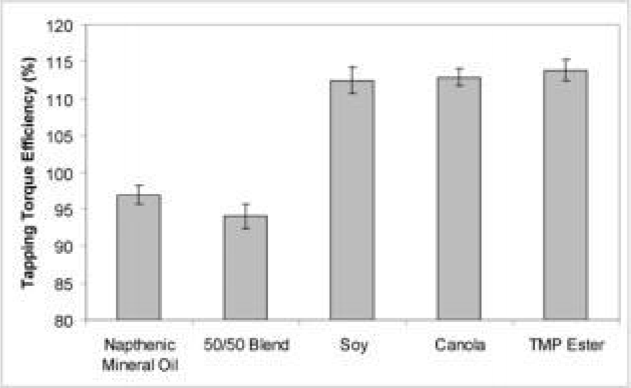

图3.五种基础油（环烷矿物油、环烷/烷烃混合油、菜籽油、大豆油及 TMP 酯）作为直链油（100%重量百分比）时的抽吸扭矩效率。

对于这些基础油的可溶性油（3.4%重量比）和半合成油（0.75%重量比）配方，研究发现石油基油与植物油在抽油扭矩效率方面的差异显著缩小。然而与矿物油基微乳液相比，植物油仍展现出明显更高的抽油扭矩效率。值得注意的是，尽管配方中油浓度明显较低，矿物油半合成微乳液的性能表现却与可溶性油基微乳液几乎不相上下。图4展示了五种油类作为可溶性油和半合成乳液时的抽油扭矩效率数据。可以看出，与图3相比，基本趋势保持不变。

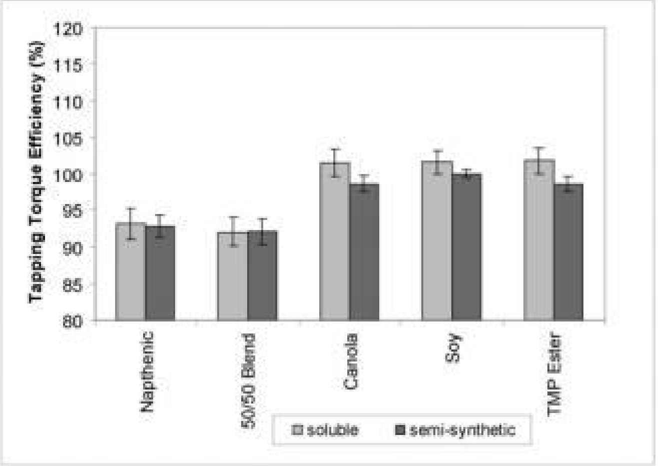

图4.五种基础油（环烷矿物油、环烷/烷烃混合油、菜籽油、大豆油及 TMP 酯）作为可溶性油（3.4%重量百分比）和半合成油（0.75%重量百分比）乳化液时的抽吸扭矩效率。

为验证硬质钢切削工艺及替代工具（CrN涂层钢）应用中的趋势，我们通过T^3试验对4140钢工件进行了三种可溶性油液（基于大豆油、矿物油和 TMP 酯）的测试（图5）。图5显示，对4140钢进行攻丝时获得的结果与对1018钢攻丝时的结果相似（图4）。基于生物原料的流体相较于矿物油基流体展现出更高的攻丝扭矩性能。但与图2所示趋势一致的是，攻丝扭矩效率差异有所减小——这符合预期，因为涂层工具的切削分辨率普遍低于非涂层工具[9]。

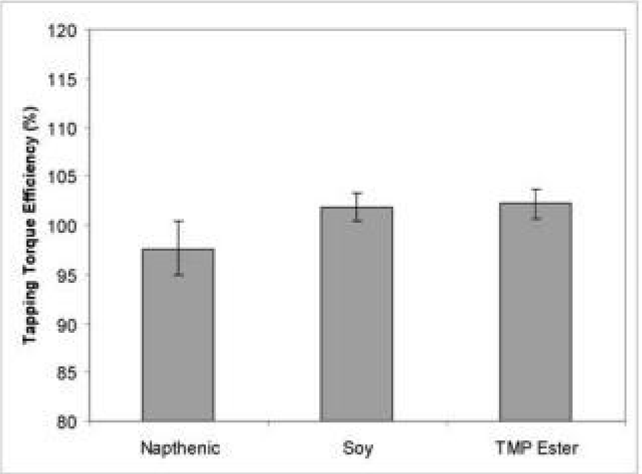

图5.三种不同基础油（环烷基矿物油、大豆油和 TMP 酯）作为可溶性油（3.4%重量百分比）在4140钢工件上的攻丝扭矩效率对比。

结果：次级添加剂对润滑性的影响

图3-5提供了表1中所列基础油（包括其乳化非离子表面活性剂和阴离子表面活性剂）在抽油扭矩效率方面的对比。此外，本研究还进行了实验，以了解除所谓“极端压力”EP添加剂外的其他二次 MWF 成分是否可能对基础油-水乳液中观察到的抽油扭矩效率产生主要影响。总体而言，MWFs含有大量二次成分，可能包括偶联剂（用于澄清 MWF 外观）、缓蚀剂、螯合剂（用于抵消硬水离子的不稳定影响）、pH缓冲剂等。

如采用辅助成分配制时，一种在既往研究中经过广泛验证的半合成 MWF 具有以下组成[5]：57重量%去离子水、1.5重量%偶联剂（丁基卡比醇）、3.7重量%松香脂肪酸、7.9重量%缓蚀剂（单乙醇胺）、15重量%油类、14重量%表面活性剂。如图6所示，这些辅助成分的存在似乎对环烷基 MWF 基础乳液的抽油扭矩效率无显著影响。鉴于作者在其他矿物水基液（MWF）中也观察到类似结果，这表明图3-5所示数据对其代表的基础流体具有普遍适用性。但需注意的是，该研究未对实验中未涉及的EP添加剂对抽油扭矩效率可能产生的影响进行评估。关于EP添加剂在创新 MWF 配方中的潜在作用，将在下一章节展开讨论。

讨论：EP添加剂对T^3的影响

极端压力（EP）润滑是磨料水基液（MWFs）中常见的固膜润滑形式，其固膜通过EP添加剂在切削加工过程中的极端压力与温度条件下产生的腐蚀作用形成。如图7所示，MWFs中使用的EP添加剂为水不溶性有机化学品（通常为有机磷化合物）。

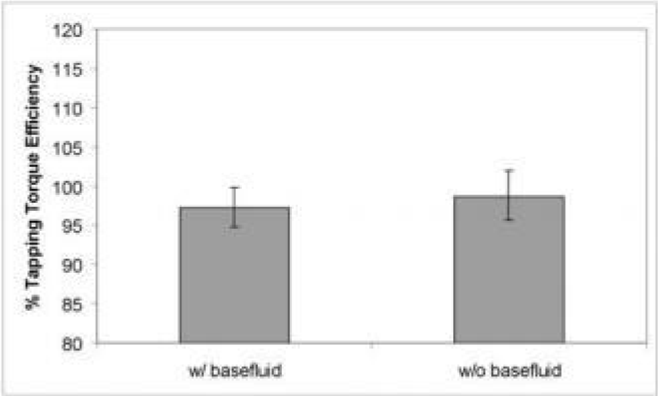

Figure 6. Tapping torque efficiency for naphthenic oil in water emulsions at semi-synthetic oil concentrations with and without secondary additives (butyl carbitol, fatty acid, monoethanolamine).

chlorine, or sulfur compounds) that decompose under extreme pressure-temperature conditions to form films of high melting point metal oxides and salts (of phosphate, chloride, and sulfide) on the tool and workpiece surfaces. These films have low shear stress and prevent direct metal-to-metal contact [11].

The choice of EP additives in a MWF depends on the temperature local to the cutting zone. Pressures in the cutting zone can be as high as 200 N/mm^2 for nonferrous metals and low-carbon steels to 1500 N/mm^2 for difficult-to-machine materials, and even higher for hardened steels [12]. In such cases, the temperature in the cutting zone can range from 350° C to above 1000° C due to the heat generated from metal deformation (in the metal shearing zone of the cut) and from friction between the chips and tools along the tool face as the cut metal is ejected from the cutting zone [11]. Since the mechanisms of EP additive effectiveness depends on the formation of metal oxides and salts, EP additive effectiveness depends on the local temperature. Generally, the temperature of EP additive activity for organo-phosphorous compounds ranges from 200-500° C. For organo-chloride compunds the range is 500-800° C, and for organo-sulfur compounds the range is 700-1000° C. As a single cut can span the full range of these temperatures as a function of the distance from the cutting zone, a suite of EP additives that span the whole range of temperatures may be found in a MWF formulation.

In order to be effective, EP additives must dissolve in the MWF formulation and reach the appropriate surfaces during the cutting process. In semi-synthetic and soluble oil MWFs, the oil-in-water emulsion provides the needed hydrophobic host for the EP additives, since the nearly all the additives have limited solubility in water but very high solubility in oil. However, the EP additives must also get to the surface to produce effective lubrication films. Because semi-synthetic and soluble oil MWFs possess a variety of surface active emulsion stabilizing agents, an effective means for delivery is available. Specifically, the surfactants that stabilize the emulsion also produce organic films on the metal surfaces that provide a hydrophobic host for EP additives to partition into. EP delivery to the surface is thus accomplished by the transfer of the oil, EP additives, and other hydrophobic organic materials from the emulsion droplets to the organic films formed on the solid surfaces. More investigation is necessary to better understand the relationship between the selection of EP additives and their synergistic/antagonistic relationship with the balance of MWF formulations.

Results & Discussion: Impact of Particle Size on Lubricity

To avoid confounding the tapping torque efficiency results in Figures 3-5, the base emulsions in Figures 3-5 were not formulated with EP additives or secondary additives. Interestingly, while the soy and canola straight oils featured approximately the same tapping torque efficiency (Figure 3), the soy based MWF had slightly higher tapping torque efficiency in the semi-synthetic form (Figure 4). In the course of the research, it was questioned whether this might be due to the smaller particle size of the canola oil semi-synthetic (~0.6µm mean particle diameter) relative to the soy oil semi-synthetic (~1µm mean particle diameter). While it is known in metal forming operations such as rolling that such particle size considerations can be quite important, a similar investigation has not been described in the literature looking at this issue for a metal cutting operation such as tapping. Since anecdotal evidence has also suggested that emulsion droplet (or "particle") size can also impact the bioresistance of a metalworking fluid, this issue was also investigated.

Figure 8 illustrates the relationship between increasing emulsion droplet (or "particle") diameter, tapping torque performance, and microbial load for a naphthenic- semi-synthetic MWF formulation after the addition of calcium hydroxide [10]. A mean emulsion size shift from 20 to 2000 nm was observed and led to a slight, albeit statistically significant, improvement in tapping torque efficiency. Interestingly, the same emulsion particle size shift increased the total microbial load in the MWF by nearly 440%.

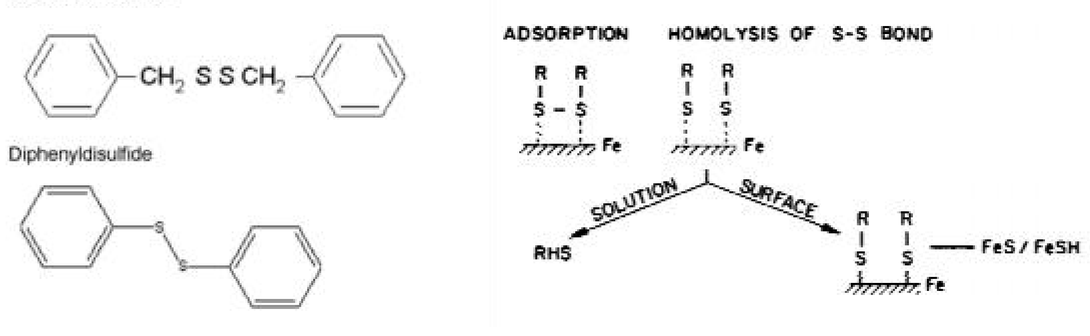

Figure 7. (Left) Two candidate organo-sulfur EP additives for MWFs: dibenzyl disulfide and diphenyldisulfide. (Right) Proposed mechanism of organo-sulfur action in metal cutting after Bushan (1999) [11].

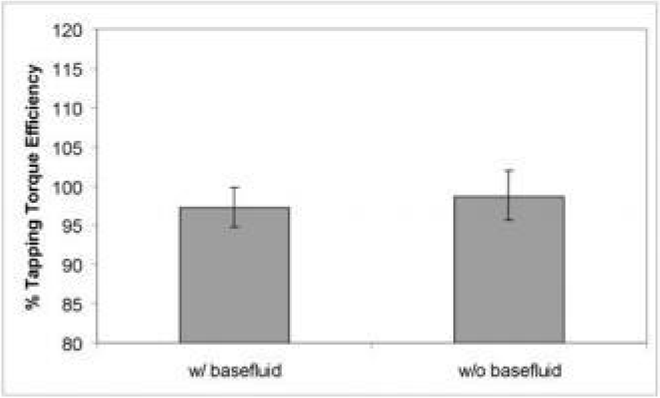

图6. 半合成油浓度下含环烷油水乳液的抽吸扭矩效率（含/不含二次添加剂：丁基卡比醇、脂肪酸、单乙醇胺）

氯或硫化合物）在极端压力-温度条件下分解，在刀具和工件表面形成高熔点金属氧化物及盐类（磷酸盐、氯化物和硫化物）薄膜。这些薄膜具有较低的剪切应力，可防止金属与金属直接接触[11]。

MWF 中EP添加剂的选择取决于切削区域的局部温度。切削区域的压力对于有色金属和低碳钢可高达200 N/mm^2，对于难加工材料可达1500 N/mm^2，而对于硬化钢则更高[12]。在此情况下，切削区域的温度范围可从350。C至高于1000。切削过程中，金属变形（在切削区域的金属剪切带） 以及切削金属从切削区弹出时切屑与刀具表面之间的摩擦所产生的热量 ，是导致切削效率降低的主要原因[11]。由于电火花加工添加剂的效能机制依赖于金属氧化物和盐类的形成，其效果与局部温度密切相关。通常而言，有机磷化合物的电火花加工添加剂活性温度范围为200-500℃。。C. 对于有机氯化合物，其范围为500-800。C，对于有机硫化合物而言其范围为
温度范围为。700-1000℃。 由于单次切割可随与切割区域距离的变化覆盖整个温度区间，因此 MWF 配方中可采用覆盖全温度范围的EP添加剂组合。

要实现有效润滑，EP添加剂必须溶解于 MWF 配方中，并在切削过程中到达目标工件表面。在半合成油和可溶性油基金属加工液中，水包油乳液为EP添加剂提供了所需的疏水基质——几乎所有添加剂在水中溶解度有限，但在油中溶解度极高。然而EP添加剂还需抵达表面以形成有效润滑膜。由于这类油基加工液含有多种表面活性剂和乳液稳定剂，其输送机制具有独特优势。具体而言，稳定乳液的表面活性剂会在金属表面形成有机膜层，为EP添加剂提供可渗透的疏水基质。通过油液、EP添加剂及其他疏水性有机物质从乳液液滴向固体表面有机膜层的转移过程，实现了EP成分向工件表面的精准输送。未来仍需深入研究EP添加剂的选择与MWF 配方平衡状态之间的协同/拮抗关系，以优化配方设计。

结果与讨论：粒径对润滑性的影响

为避免图3-5中拔拔力矩效率结果产生混淆，这些图表中的基础乳液均未添加EP添加剂或二次添加剂。值得注意的是，虽然大豆油和菜籽油直馏油的拔拔力矩效率相近（图3），但半合成大豆油基 MWF 在拔拔力矩效率方面略胜一筹（图4）。研究过程中，我们推测这可能源于菜籽油半合成油（平均粒径约0. 6μm）相较于大豆油半合成油（平均粒径约 1μm）的颗粒尺寸更小。尽管在轧制等金属成形工艺中，颗粒尺寸因素已被证实具有重要影响，但针对拔拔等金属切削工艺的类似研究尚未见文献记载。基于坊间证据表明乳液液滴（或称“颗粒”）尺寸同样会影响金属加工液的生物相容性，本研究对此问题也进行了深入探讨。

图8展示了添加氢氧化钙后，环烷基半合成 MWF 配方中乳液液滴（或称“颗粒”）直径增大、抽吸扭矩性能与微生物负载之间的关系[10]。观察到乳液平均粒径从20纳米增至2000纳米，导致抽吸扭矩效率虽提升幅度较小但具有统计学显著性 。值得注意的是，相同乳液粒径变化使 MWF 中的总微生物负载量增加了近440%。

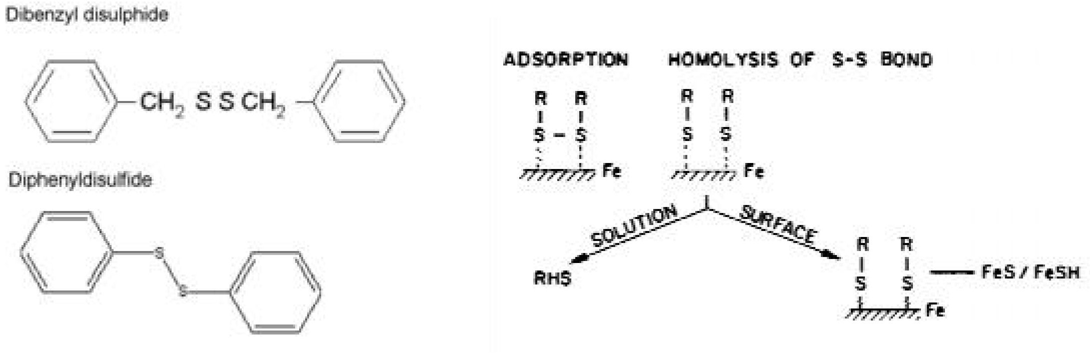

图7。（左）两种适用于金属加工液（MWFs）的候选有机硫EP添加剂：二苄基二硫化物与二苯基二硫化物。（右）基于Bushan（1999）[11]提出的金属切削过程中有机硫作用机制示意图。

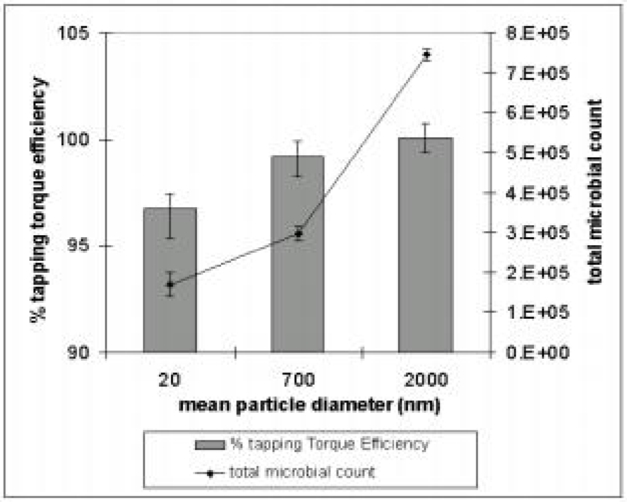

Figure 8. Tapping torque efficiency and microbial count as a function of mean particle size diameter for a naphthenic semi-synthetic MWF after Zimmerman et al. (2004) [10]

The reduction in bioresistance, and the increase of tapping torque efficiency, are likely to be due to the physical size of the MWF emulsion, rather than the addition of calcium. For the case of bioresistance, it is known that calcium is not typically a limiting nutrient in aqueous systems such as MWFs [13]. For the case of tapping torque efficiency, it is known that calcium contains no inherent lubricity characteristics. Particle size was shown to increase in the presence of other ions (e.g. magnesium) with similarly small increases in tapping torque efficiency [10]. Fluids at the same ion concentration had statistically identical tapping torque performance indicating that the final particle size determines the machining performance of the MWF regardless of the cause of the particle size shift. This suggests that particle size could be playing a role in the tapping torque efficiency differences observed between the straight oil and semi-synthetic MWF formulations for the soy versus canola base oils.

SUMMARY AND CONCLUSIONS

This study has used the tapping torque test to compare the performance of five base oil feedstocks for MWFs: naphthenic mineral oil, a 50/50 blend of naphthenic and paraffinic mineral oil, soybean oil, canola oil (75% oleic content), and a TMP Ester. The five oils were tested as straight oils, and formulated into soluble oil and semi-synthetic MWFs, to understand the impacts of emulsification on base oil performance. The results indicate that as straight oils, all vegetable based stocks, and the vegetable based ester, perform significantly better than the mineral oils. This trend holds, although is much less pronounced, after the vegetable stocks are emulsified into soluble oil and semi-synthetic MWFs. The results also indicate that some vegetable oil base stocks have a higher potential for lubricity than others, with data revealing that the soy and TMP ester provide improved tapping torque efficiency relative to canola oil in emulsified MWFs. Additional analysis suggests that such differences, although minor, may be related to the mean particle diameter of the MWF emulsions.

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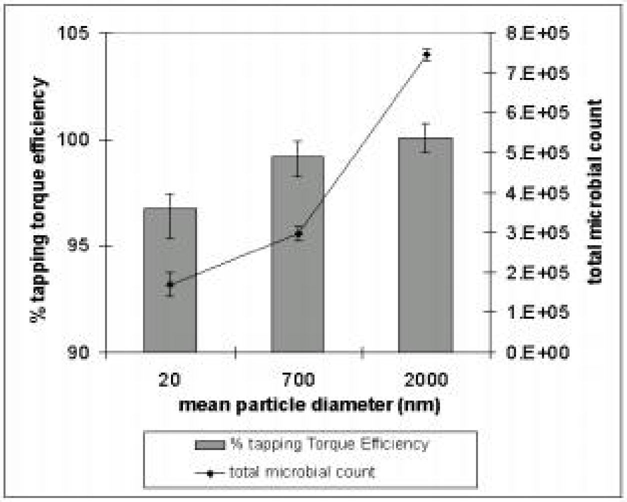

图8.环烷系半合成 MWF 的抽吸扭矩效率与微生物计数随平均粒径变化关系（Zimmerman 等，2004）[10]

生物抗性降低与抽吸扭矩效率提升的现象，更可能源于 MWF 乳液的物理尺寸而非钙元素的添加。就生物抗性而言，已知钙元素在中水处理厂等水性体系中通常并非限制性营养物质[13]。关于抽吸扭矩效率方面，钙元素本身并不具备润滑特性 。研究显示，当存在其他离子（如镁离子）时，颗粒尺寸会增大，但抽吸扭矩效率仅出现微小增幅[10]。相同离子浓度下的流体在抽吸扭矩性能上呈现统计学上的完全一致，这表明最终颗粒尺寸决定了 MWF 的加工性能，与颗粒尺寸偏移的成因无关。这表明颗粒尺寸可能在大豆基油与油菜籽基油中，直链油与半合成 MWF 配方间观察到的抽吸扭矩效率差异中起着关键作用。

总结与结论

本研究采用击打扭矩测试法对比了五种矿物油基础油原料的性能表现：环烷基矿物油、环烷基与石蜡基矿物油50/50混合油、大豆油、菜籽油（油酸含量75%）以及 TMP 酯。通过将五种基础油分别作为直链油进行测试，并配制成可溶性油和半合成矿物油基润滑液，以探究乳化作用对基础油性能的影响。结果表明，作为直链油时，所有植物基原料及植物基酯类产品的性能均显著优于矿物油。当植物基原料被乳化为可溶性油和半合成矿物油基润滑液后，这一趋势虽有所减弱但仍持续存在。数据还显示部分植物油基础油具有更高的润滑潜力——在乳化矿物油基润滑液中，大豆油和TMP 酯相较于菜籽油展现出更优异的击打扭矩效率 。进一步分析表明，这些差异虽微小，可能与 MWF 乳液的平均粒径参数相关。

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