KSTLE International Journal, Vol. 4, No. 2, December 2003, pp. 52-54

Analysis on Chemical Ingredients with Anti-microbial Activity in Water-based Metalworking Fluids

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Abstract: This study was conducted to estimate if the level of several chemical ingredients including alkanolamines or ethanolamines (EA) examined in the specific synthetic metalworking fluid (MWF) "A" can cause anti-microbial activity and health effect. Three water-based MWF products ("A", "B", and "C") were studied every week for two months (from June 1, 2002 to July 30, 2002). Chemical ingredients such as formaldehyde, boron, EA, and copper were examined. In the sump where MWF "A" was used, not only the total level of EA, monoethanolamine(MEA), diethanolamine(DEA) and triethanolamine(TEA), but also boron level were significantly higher than those of the other MWFs. ANOVA statistical tests indicated that levels of pH, alkalinity, boron, MEA, DEA and TEA in MWF "A" were significantly higher than those in other MWF types. Correlation tests also found that levels of pH, alkalinity, boron, MEA, DEA and TEA in MWF "A" are significantly correlated. We suggested the assumptions that excessive concentrations of EA, and borate at a high pH level, may cause anti-microbial resistance synergically. To demonstrate this assumption, additional study is needed to examine the relationship between the levels of microbes and excessive concentrations of EA, and borate at a high pH level.

Keywords: Synthetic metalworking fluids, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (MEA)

Introduction

Metalworking fluids (MWFs) are fluids used during machining and grinding to prolong the life of the tool, carry away debris, and protect the surfaces of work pieces [1]. There are four different classes of MWFs: straight MWFs, soluble oil MWFs, semi-synthetic MWFs and synthetic MWFs. MWFs except for straight are all water-soluble fluids because they are diluted with water. A wide variety of chemicals may be used in each of the MWF classes. The risks these chemical pose to workers may vastly vary because of different manufacturing processes, various degree of refining, recycling, improperly reclaimed chemicals, different degree of chemical purity, and potential chemical reaction between components. Limited information exists about the chemical components of specific MWFs because of the highly competitive and proprietary nature of the metalworking industry [1].

Water-based MWFs are excellent nutritional sources for many kinds of bacteria and fungi.

A specific synthetic MWF (designated as MWF "A"), imported from Japan, was acclaimed to have excellent anti-microbial activity. The owner of this machine shop determined that risk of MWF "A" needs to be assessed before it is introduced to other sumps. We were asked to evaluate whether the use of this fluid is appropriate for both worker health and operation.

The Material Safety Data Sheets (MSDS) on MWF "A" indicated only a presence of carboxylic salts, synthetic oil, and EA. The specific amount and type of EA were not addressed due to confidential trade secrets. The MSDS was not a useful reference for the presence, or relative amount of components. Alknanolamines or ethanolamines (EA) such as monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) may be used in soluble MWFs in order to stabilize pH or inhibit corrosion. Workers exposure to EA has been reported to cause acute allergic responses including dyspnea and asthma. In addition, case reports have linked exposure to EA with asthma in certain occupational settings [2].

This study was conducted to examine if their levels in a specific synthetic metalworking fluid (MWF) "A" can cause anti-microbial activity and health effect.

To accomplish this purpose, several chemical ingredients that were suspected to have anti-microbial performance were investigated and compared among MWFs.

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Methods

MWF type and sump studied

Three types of water-based MWFs (MWF "A", "B" and "C") were studied every week for two months (from June 1, 2002 to July 30, 2002) in a single machine shop. MWF "A", a synthetic type, was first charged to one sump called MT 01 on September 1, 2001. This MWF had been used without replacement until July 30, 2002, the end of this study. Two other products of soluble MWFs ("B" and "C") were used in six other sumps, for both longer and shorter periods than the synthetic MWF "A", again without changing the fluid.

MWF sump bulk sample collection and measurement

One fluid sample from each sump was taken once every week. The pH levels of the MWFs were measured in the field using a thermometer (model 230, Portable Meter, ORION). In addition, the MWF concentration was measured in the field using a refractometer (model, ATAGO N20E, Japan). Total alkalinity was analyzed in laboratory according to "method No. 2320 A" of the "Standard Methods for Examination of Water and Wastewater" [3].

Formaldehyde

Formaldehyde, released from formaldehyde liberating biocide in the bulk sample, was quantified by reacting with 2,4DNPH, which resulted in the formation of formaldehyde-2.4 DNPH derivatives. After this derivative was desorbed in acetonitrile 1 ml (Merck, HPLC grade, Germany), it was analyzed by an HPLC UV-VIS absorbance detector (model, Waters Alliances, USA). A standard curve to quantify the formaldehyde in the MWF, was constructed by serial dilution of formaldehyde-DNPH stock solution (100 mg/ml in acetonitrile, Cat No. 4-7177, USA).

Element analysis: boron and copper

The MWF bulk sample was pretreated by microwave (model MDS-2000; CEM Corp., USA). Copper and Boron compounds in the MWFs were quantified as elements using Inductively Coupled Plasma (model OPTIMA 3,000 DV, Perkin Elma). An external quality control program for metals was performed through participation in the Proficiency Analytical Testing (PAT), organized by the US National Institute for Occupational Safety and Health (NIOSH)/ American Industrial Hygiene Association (AIHA). Our results were always evaluated as acceptable.

Monoethanolamine (MEA), di-(DEA) and tri-(TEA)

A portion of MWF sample was filtered using a micro-syringe, with a 0.4 μm pore size filter, and quantified by ion chromatography (WATERS, Waters, USA) equipped with composed of a guard column (IC PAK^{Tm} C M/D, USA), column (IC PAK^{Tm} Cation M/D column, USA), and a detector (432 conductivity detector, Waters, USA). An eluent of 0.1 mM EDTA and 2 mM nitric acid was filtered through a Super 450 membrane filter (Waters, diameter 47 mm, pore size 0.45 μm, USA), and sonicated using a sonicator (Branson, 3210), for 40 minutes to remove dissolved air. Samples for quantification were diluted in order to allow them to reach optimum levels for analysis.

Statistical analysis

Statistical testing was carried out using SPSS standard version. Correlation tests among pH, MWFs concentration and chemical ingredients in MWFs were computed. ANOVA test was performed to compare the differences of chemical ingredients levels among MWF types.

Results

The study results on pH level, MWF concentration, alkalinity and chemical components by MWF types are indicated in Table 1. The pH level of the MWF "A" ranged from 9.01 to 9.38 (average: 9.14) and was significantly higher level than those in other sumps. Total alkalinity ranged from 15,200 ppm to 14,700 ppm, which was far higher than the range of other sumps, 1,300 ppm-5,200 ppm. Correlation tests indicated EA levels are significantly correlated with alkalinity concentration (Table 2). This result demonstrated that high alkalinity in MWF "A" may result in high pH.

The levels of alkalinity, boron and EA are compared in Fig. 1. Elemental concentrations of boron in the MWF "A" were also significantly higher than those in other MWFs. The average of total EA in MWF "A" (range: 35,595 ppm to 57,857 ppm). This level was over ten times higher than the averages in MWF "B" and "C". Furthermore, concentrations of MEA, DEA and TEA were also significantly higher than those in other sumps. In particular, TEA accounted for 84% of the total EA. Total level of EA ranged from 35,595 ppm to 57,857 ppm. ANOVA statistical tests showed that levels of pH, alkalinity, boron, MEA, DEA and TEA in MWF "A" were significantly higher than those in other MWF types (Table 1and Fig. 1). Correlation tests also found that correlation among levels of pH, alkalinity, boron, MEA, DEA and TEA in MWF are significant (Table 2).

Discussion

Historically, microbial contamination of MWFs has been a problem in the metalworking industries, primarily because of microbial growth effects on fluid quality and performance [1]. Chemical additives such as biocide are added in water-based MWFs to prevent excessive microbial growth. In particular, information on amount and components of chemical ingredients contained in MWF were not fully addressed on MSDS.

Our results of pH level and MWF temperature indicated that all MWFs provided appropriate environmental conditions for microbial growth. Although the synthetic MWF "A" had been used without replacement for 12 months, fluid contamination from microorganisms had not been found.

As was indicated Table 1and Fig. 1, the levels of EA, alkalinity and boron between MWF "A" and the other MWFs ("B" and "C") were significantly different. In particular, high

Table 1. Summary of levels in bulk sump samples of water-based metalworking fluids (MWF "A" used in sump MT 01, MWF "B" in two sumps, and MWF "C" in four sumps)

	MWF "A"		MWF "B"		MWF "C"		ANOVA	
	Sample No.	Average(SD)	Sample No.	Average(SD)	Sample No.	Average(SD)	F-ratio	p-value
MWF pH	8	9.14 (0.12)	16	8.64 (0.50)	32	8.92 (0.42)	4.25	0.019
MWF Temperature (°C)	8	22.6 (3.6)	8	24.0 (3.18)	32	23.4 (3.09)	0.261	0.773
MWF concentration (%)	8	6.2 (0.65)	16	5.4 (1.49)	32	7.0 (2.56)	3.003	0.055
Alkalinity, mg/l	8	13,838 (941)	16	2,869 (695)	32	3,497 (964)	480.9	0.000
Boron, mg/l	8	105.1 (13.9)	13(3) [1]	12.7 (8.9)	28(4) [1]	14.4 (13.9)	171.3	0.000
Copper, mg/l	1 (7) [1]	0.2	16	12.4 (6.9)	30(2) [1]	25.9 (17.6)	5.265	0.009
Formaldehyde, mg/l	8	285 (58)	32	311 (150)	32	95 (112)	0.451	0.991
MEA, ppm	8	4,036 (687)	5 (11) [1]	680 (437)	20(12) [1]	1,296 (614)	73.86	0.000
DEA, ppm	8	2,386 (384)	0 (16) [1]	not detected	2(30) [1]	971 (583)	7.053	0.017
MEA, ppm	8	34,480 (6,537)	15 (1) [1]	520 (377)	32	1,229 (651)	680.2	0.000
Total ethanolamine, ppm	8	40,903 (6,888)	15 (1) [1]	622 (714)	32	2,003 (1,378)	742.8	0.000

Sample number: Number of sumps where each type of MWF was used x8 measurements

[1]: Sample number in parenthesis = number of sample not detected, average and standard deviation were from results of samples detected.

MEA: Monoethanolamine, DEA: Diethanolamine, TEA: Triethanolamine

Table 2. Correlation matrix among chemical ingredients in MWFs

	MWF conc	pH	Boron	Copper	Alkalinity	MEA	DEA	TEA
MWF conc.	1	0.38	-0.21	0.83**	0.06	0.28	-0.06	-0.03
pH		1	0.53	0.03	0.51	0.73**	0.51	0.52
Boron			1	-0.64	0.94***	0.84**	0.97***	0.97***
Copper				1	-0.41	-0.16	-0.47	-0.47
Alkalinity					1	0.93***	0.99***	0.99***
MEA						1	0.91***	0.92***
DEA							1	0.99***
TEA								1

***: $p<0.01$

**: $0.01<p<0.05$

MEA: Monoethanolamine, DEA: Diethanolamine, TEA: Triethanolamine

level of EA and alkalinity were found in MWFs "A". Excessive amount of EA may result in high level of alkalinity. It could be suggested that abuse of EA and boron could contribute to strong anti-microbial performance in MWFs. The levels of EA we investigated were far higher than those reported on MSDS. Boron was not addressed on MSDS. This results demonstrated that MSDS was not useful for workers right to know toxicity of ingredients in MWF "A".

There have been several studies stating that TEA, DEA, and MEA inhibit the growth of a wide variety of microorganisms [4-8].

Sandin *et al.* (1990) found that the anti-microbial effects of alkanolamine such as DEA are greatly enhanced at a high pH. A reduction of more than 10^5 CFU/ml, compared with uninhibited growth, was found at pH 9.1 for 76 mM DEA [6], corresponding to 7,990 ppm. Based on the results, they proposed the alkanolamine compound as an appropriate anti-microbial agent for use in alkaline MWF [6]. Rossmoore (1993) studied the dual role of pH and EA in contribution to bio-stability in MWF, and found that a high pH (i.e., about 10) produced a degree of bio-stability [9]. Hernandez *et al.* (1984) reported the anti-microbial performance by boron-amine interaction with three types of synthetic formulations. However, neither boron nor EA alone produced the desired anti-microbial results. Both amine and borate-based, one with a pH of 9.8 and the other with a pH of 9.2, showed complete control of bacterial growth for eight weeks [9].

Our study found significant difference in pH, boron, MEA, DEA and TEA between MWF "A" and the other two MWF (Table 1). Statistical tests indicated that the levels of pH, boron, MEA, DEA and TEA were significantly correlated (Table 2).

These study results suggest the assumption that a high EA level in combination with borate at a high pH (9.01-9.38) can lead to anti-microbial resistance in MWF "A".

However, it is very difficult to find appropriate levels of EA and boron that can prevent not only excessive microbial growth in MWF "A", but also workers health.

The TEA average level (34,480 ppm) in synthetic MWF "A" greatly exceeded 2.5% of threshold amount that the Independent Lubricating Manufacturing Association (ILMA)

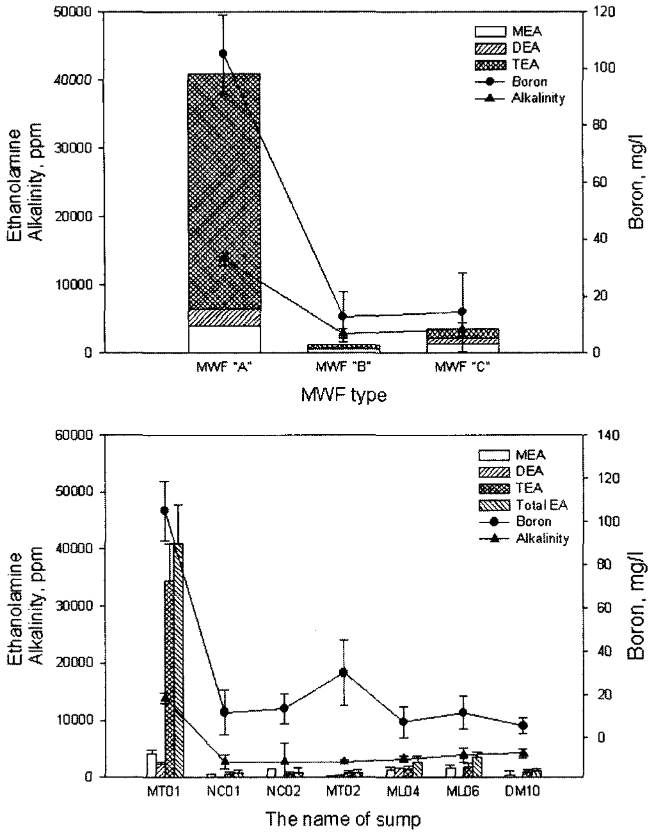

Fig. 1. Comparison of boron, alkalinity and Eas by MWF type and sump (MT01; MWF "A", NC01 & NC02; MWF " B", MT02, ML04, ML06 & DM10; MWF "C"). MEA: Monoethanolamine, DEA: Diethanolamine, TEA: Triethanolamine

has recommended based on the calculation of exposure risk [4]. The MEA and DEA levels examined in MWF "A" also exceeded this threshold.

Although EA might improve anti-microbial performance, it is certain that excessive amounts of EA can cause adverse health effects. EA has been associated with respiratory irritant and a sensitization [2].

Manufacturer has to design MWFs that can be both microbiologically resistant in use, as well as nontoxic. It is not easy work to develop MWF satisfied with these dual goals. Water-based MWF that may include base oils (synthetic, semi-synthetic, petroleum oil), water, emulsifiers, preservatives and other additives, eventually undergo microbial degradation. However, it is technically impossible for end users to evaluate a manufacturers claims that their fluids are resistant and therefore, do not require biocide additions. Our study also addresses a really important issue in the failure to report ingredients on the MSDS.

Legal action should be taken to regulate the total levels of EA and boron in MWFs.

Conclusions

Our study found that levels of pH, alkalinity, boron, MEA, DEA and TEA in MWF "A" were significantly higher than those in other MWF types and correlated. Abuse of EA and boron could contribute to strong anti-microbial performance in MWFs. These study results suggest the assumption that a high EA level in combination with borate at a high pH (9.01-9.38) can lead to anti-microbial resistance in MWF "A". Future research is needed to examine whether excessive concentration of EA, and borate at a high pH level may cause anti-microbial activity. For this study level of microbes that can be regarded as contamination indicator should be analyzed.

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