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HUMAN HEALTH CONCENRS OF THE METALWORKING FLUID COMPONENTS (Part II – Biocides, corrosion inhibitors and neutralizing agents)

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Abstract

The exploration of 209 available Material safety data sheets of 85 straight oils, 46 emulsions, 51 semi-synthetics and 27 synthetics was carried out to provide a report on the most used components defined as dangerous substances. As many as 217 of different substances of which 15 were identified as biocides, 17 as corrosion inhibitors or neutralizing agent, 17 were lubricity improvers and 38 different base fluids, lubricity solvents or surfactants, while 93 substances were not identified specifically and 37 substances occurred only once. This article is focused on the list of biocides, neutralizing agents and corrosion inhibitors identified in all types of MWFs and their possible health effects.

Key words

Metalworking Fluids, Composition, Exposure, Health effects, Biocides, Corrosion inhibitors

INTRODUCTION

Worldwide annual consumption of MWFs is estimated at more than 2×10^9 l. However, the waste of used MWFs may be up to 10 times higher, which is due to the fact that most MWFs must be diluted before use (1). Workers in machining environments are exposed to numerous substances and conditions that may affect their health and safety (2). Each component of MWF may contribute to health effects, and hence the nature and severity of any health effects depends to some extent on the specific composition of the MWF and the specific metalworking operation in which the fluid is applied (3). Exposure of operating staff to MWFs occurs as inhalation of aerosols or by skin contact – touching contaminated surfaces, using parts and equipment, fluids splashing, and aerosol deposition on the skin. Inhalation of MWF aerosols can cause irritation of the throat (pain, burning throat), nose (rhinorrhoea, congestion, and nosebleeds) and lungs (cough, shortness of breath, increased mucus production). MWF aerosol exposure is often associated with chronic inflammation of the bronchi (bronchitis), hypersensitive pneumonitis, and deterioration of existing breathing problems (asthma) (4). Information about the adverse health effects associated with occupational exposure to MWF can be found in (5-8). A significant role in the development of these diseases has a low level of sanitation, failure of hygienic standards and underestimation of the risk by workers (4).

Strategy to Reducing the Exposure

Effects of MWFs Reducing the MWF effects in the work environment is carried out by generally known principles of preventive medicine work: a) By reducing the concentration (dose) and/or b) By reducing exposure (duration, repetition, and frequency). Technical and organizational (collective) actions are primarily applied. Technical actions include reducing the amount of MWFs, e. g. by technological change of process, more effective local exhaust or general room ventilation and careful ongoing maintenance of equipment and process control. Organizational actions include: reducing the number of employees and their rotation at risk job, correct regime of work and relaxation (frequent breaks out of the risk areas), regular monitoring of pollutant concentration in the working environment, and performance of health surveillance, etc. Compensatory (individual) actions (e. g. use of personal protective equipment – breathing masks or respirators with an effective filter suitable for mist containing oil, gloves, goggles, etc.) are applied in the second place if there is no possibility to avoid exposure (4).

Biocides

Biodeterioration of MWFs which is due to microbial contamination has several detrimental effects. It changes the stability of the emulsion by altering fluid viscosity, increases the rate of corrosion leading to leaks in MWF systems and reduces tool life. Biofilms and fungal growth may cause clogging of the machining systems (9). There are many potential sources of the microbial contamination of MWFs. Microorganisms may be introduced into the coolant with water used as a diluent. The microorganisms that have survived washing procedures and disinfection of tanks in the form of biofilms can resettle and multiply in distribution systems. Microbes also penetrate into the cooling system on metal parts that are used in the processing (10). Additionally MWFs are contaminated by the workers themselves through bacteria from the skin, waste, food, drinks as well as contaminated workpieces and surfaces (11). Huge variety of microorganisms can pose a risk for the health of workers, since inhalation of aerosols can lead to hypersensitivity pneumonitis and chronic obstructive pulmonary disease, as well as other respiratory and skin diseases (12). The use of biocides (also known as antimicrobial pesticides) is the most common method for controlling microbiological growth in MWFs. The use of biocides reduces or maintains bacteria and fungi at acceptable levels and ultimately maintains the integrity of the final product (13). Biocides are usually incorporated into MWF formulation by the manufacturer, or to the dilution at the tank side (14, 15). Levels of preservatives in the metalworking fluid must be kept sufficiently high in order to maintain efficacy against micro-organisms (15). The commonly used biocides for prevention of microbial contamination are phenol derivatives, agents realizing formaldehyde, glutaraldehyde, sodium pyridine-thiol oxide, isothiazolinones and alkanolamines. Alkanolamines are used in metal working fluids as corrosion inhibitors, but they have also antimicrobial effect. The antimicrobial effect of ethanolamines is suggested to be due to their surface-active properties or due to the alkanolamines damage the cell membrane (16). Although, effective action of biocides against microorganisms requires prolonged application, often with application in high concentrations, which often causes allergic reactions in machine operators, as they are highly sensitizing chemical compounds (17). Governmental agencies in most countries regulate the use of biocides. In the United States, biocides are regulated by the Environmental Protection Agency (EPA), under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and must meet certain toxicological and environmental impact standards. Biocides are approved based on the relative risk resulting from their use. In the European Union, the Biocidal Products Directive (BPD, Regulation (EU) 528/2012) performs a similar function (13).

From the review of 209 available MSDS, about 15 biocides/fungicides substances were identified occurring 101 times. The most frequently listed biocides and fungicides are presented in Table 1.

Table 1 The most frequently listed biocides and fungicides

	Occurrence [%]	**Concentration in the concentrate [%]**	**BPR -** Biocidal Products Regulation	**EPA-FIFRA Registration Process**
Aldehyde derivatives:				
CAS 66204-44-2 N,N′-methylenebis[5-methyloxazolidine] (MBO)	27	1-5	PT 13 under review	Pending Registration
CAS 3586-55-8 1,6-dihydroxy-2,5-dioxahexane	10	1-3	PT 13 under review	No data found
CAS 5625-90-1 N,N'-Methylenebismorpholine (MBM)	10	1-5	PT 13 approved	none
CAS 4719-04-4 N,N',N''-tris(β-hydroxyethyl) hexahydro-1,3,5-triazine	8	1-5	PT 13 under review	Registration Review
Carbamates:				
CAS 55406-53-6 3-Iodo-2-propynyl butylcarbamate (IPBC)	22	0.1-1	PT 13 approved	Registration Review
Phenols:				
CAS 128-37-0 2,6-di-tert-butyl-4-methylphenol (butylated hydroxytoluene, BHT)	10	0.1-2.5	-	none
CAS 128-39-2 2,6-di-tert-butylphenol	1	-	-	No data found
Heterocycles containing N or N and O or N and S	7	-	-	
Others	1	-	-	

The most frequently occurred compounds of the biocides are MBO and IPBC, followed by the MBM, BHT and 1,6-dihydroxy-2,5-dioxahexane. Total occurrence of substances can be ascribed to the formaldehyde releasers present 45 %.

Formaldehyde has been proved to cause cancer in the laboratory animals; and the human data are equivocal. This compound is also a well-known irritant and can cause either allergic or contact dermatitis. There is additional concern that nitrated biocides may release nitrites, which are precursors for nitrosamine formation (18).

Oxazolidin/MBO (CAS 66204-44-2) is a formaldehyde releasing biocide added to coolant oils (19). According to the classification provided by companies to ECHA in CLP notifications this substance causes severe skin burns and eye damage, is harmful if swallowed, is harmful if inhaled, causes serious eye damage, is harmful in contact with skin and may cause long lasting harmful effects to aquatic life (20).

1,6-dihydroxy-2,5-dioxahexane (CAS 3586-55-8). According to the classification provided by companies to ECHA in CLP notifications, this substance causes serious eye damage, is harmful if swallowed, causes skin irritation and may cause respiratory irritation (20).

N,N'-Methylenebismorpholine/MBM (CAS 5625-90-1) belongs to a category of biocidal actives known as formaldehyde-releasers (or formaldehyde-donors). It has a high asthma hazard index (occupational asthma hazard index 0.98) using the Manchester Occupational Asthma Hazard Programme, which has a high sensitivity in identifying novel asthmagens (21). According to the classification provided by companies to ECHA in CLP notifications this substance causes severe skin burns and eye damage, causes serious eye damage, is harmful if swallowed, may cause an allergic skin reaction, causes skin irritation and may cause respiratory irritation (20, 22).

N,N',N''-tris(β-hydroxyethyl) hexahydro-1,3,5-triazine (CAS 4719-04-4). This substance is the most commonly used and most cost-effective formaldehyde-condensate biocide for metalworking fluids (13). According to the harmonized classification and labelling (CLP00) approved by the European Union, this substance is harmful if swallowed and may cause an allergic skin reaction. Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance is fatal if inhaled, causes damage to organs through prolonged or repeated exposure and causes serious eye irritation (20).

3-Iodo-2-propynyl butylcarbamate/IPBC (CAS 55406-53-6). According to the harmonized classification and labelling (ATP06) approved by the European Union, this substance is toxic if inhaled, causes damage to organs through prolonged or repeated exposure, is very toxic to aquatic life, is very toxic to aquatic life with long lasting effects, is harmful if swallowed, causes serious eye damage and may cause an allergic skin reaction.

Corrosion inhibitors and neutralizing agents

Corrosion control is one of the most important properties of metal-working fluids. It may be realized by the creation of a protective layer to prevent water and oxygen from contacting the metal part (23) or by adjusting and buffering the pH value of used fluids. In the group of neutralizing agents, there are alkanolamines (monoethanolamine - MEA, diethanolamine - DEA, triethanolamine -TEA) or isopropanolamines (monoisopropanolamine - MIPA, diisopropanolamine - DIPA) and 2-methyl-1-propanol (AMP). All of these, except DEA, are currently widely used in water-dilutable MWF concentrates to neutralize acid-functional components, while developing and maintaining alkaline pH once diluted by the end-user. These components are also sometimes added tank side to adjust and buffer the pH of in-use fluids. Commonly used amines such as MEA, TEA, MIPA or AMP have different advantages in terms of neutralization and buffering efficiencies (24). Alkanolamines include both amino and hydroxyl functional groups. Because of the amine functionality, they are basic compounds with acid dissociation constant (pKa) values in the higher pH range (>7); for example, the pKa values for MEA and TEA are 9.68 and 7.7, respectively. The common chemistries used for corrosion inhibitors include sulfonates, amine carboxylates, borates, amine borates, phosphates, amine phosphates and benzotriazoles (25).

From the review of 209 available MSDS, 17 different substances such as corrosion inhibitors or neutralizing agents were identified, occurring 84 times in total. The most frequently listed corrosion inhibitors and neutralizing agents are presented in Table 2.

Table 2 The most frequently listed corrosion inhibitors and neutralizing agents

	CAS number	Occurrence [%]	Concentration in the concentrate [%]
Boron compounds: Boric acid	10043-35-3	35	1-5
Aliphatic amines: Monoethanolamine (MEA)/ 2-aminoethanol	141-43-5	27	1-5 (< 30)
Triethanolamine (TEA)	102-71-6	10	1-5 (< 30)
Diethanolamine (DEA)	111-42-2	5	5-10
2-amino-2-methyl-1-propanol (AMP)	124-68-5	4	1-10
Dicyclohexylamine	101-83-7	2	1-5
Methyldiethanolamine (MDEA)	105-59-9	2	1-5
1-amino-2-propanol (monoisopropanolamine (MIPA))	78-96-6	1	1-5
2-((hydroxymethyl)amino)ethanol	34375-28-5	1	1-5
2-amino-1-butanol	96-20-8	1	0.1-1
Heterocycles containing N or N and O 1H-benzotriazole	95-14-7	4	0.1-5
Others		3	
Heterocycles containing N and S 1,2-benzisothiazol-3(2H)-one	2634-33-5	1	0.1-1
Aliphatic carboxylic acids and their salts (soaps)		4	

The most frequently occurred substances identified as corrosion inhibitors or neutralizing agents are the Boric acid, MEA and TEA. As it is described in (26) the occurrence of DEA is relatively low (5%).

Boric Acid (CAS 10043-35-3). In metalworking fluids, boric acid is used as a starting material for a wide range of corrosion inhibitors. This is most commonly achieved by reaction with alkanolamines. Boric acid based corrosion inhibitors are produced by additive manufacturers for sale to MWF formulators. Some formulators also use boric acid themselves. Consequently, the specific nature of the active ingredients in the corrosion inhibitors is complex and they can vary enormously in their chemistry. Given this complexity, it is a matter for individual manufacturers and formulators to determine the chemical nature of their products and to advise their downstream users accordingly. In most metalworking fluids, the borate compounds are present at a level below the threshold for classification of boric acid. In additives and a small proportion of fluids, the concentration of the active ingredient is higher, and the potential for the presence of unreacted boric acid has to be considered (27). Boric acid is identified as a substance meeting the criteria of Article 57 (c) of Regulation (EC) 1907/2006 (REACH) owing to its classification as toxic for reproduction (category 2): category in accordance with Annex I to Council Directive 67/548/EEC (28).

The Independent Lubricant Manufacturers Association has recommended using MWFs with 5% MEA or DEA and up to 25% TEA to calculate exposure risk. A typical 10:1 dilution of bulk metal working fluid with water gives a final concentration of 0.5% MEA or DEA and 2.5% TEA. Because of the continual addition of make-up water, ethanolamines tend not to concentrate in metal working fluids (18).

Monoethanolamine MEA/2-aminoethanol (CAS 141-43-5). According to the harmonized classification and labelling (CLP00) approved by the European Union, this substance causes severe skin burns and eye damage, is harmful if swallowed, is harmful in contact with skin and is harmful if inhaled. Additionally**,** the classification provided by companies to ECHA in REACH registrations identifies that this substance is toxic if inhaled, is harmful to aquatic life with long lasting effects, causes serious eye damage, is suspected of damaging fertility or the unborn child, may cause respiratory irritation, may cause an allergic skin reaction and may cause allergy or asthma symptoms or breathing difficulties if inhaled (31).

Diethanolamine DEA (CAS 111-42-2). The irritant action of DEA on the eyes can be severe. Direct contact of the pure liquid can impair vision. Irritation on the skin may be mild to moderate. The acute oral toxicity of this compound was low in test animals. The toxic symptoms include somnolence, excitement and muscle contraction (29). DEA was studied by National Toxicology Program (NTP). Under the conditions of a 2-year dermal study, there was no evidence of carcinogenic activity of DEA in male or female F344/N rats administered 8 to 64 mg/kg DEA. However, there was clear evidence of carcinogenic activity of DEA in male and female B6C3F1 mice based on increased incidences of liver neoplasms in males and females and increased incidences of renal tubule neoplasms in males. Based upon these dermal findings, there is concern regarding the carcinogenic potential of ethanolamines if delivered via the inhalation route of exposure (18). Due to a potential formation of carcinogenic N-nitrosamines, the use of DEA in water-based MWF has declined in the recent past (26).

Triethanolamine TEA (CAS 102-71-6). TEA is a common constituent in all cutting fluids causes asthma and is carcinogenic (30). The National Cancer Institute nominated TEA for study by NTP because of its widespread use in consumer products, its high potential for worker exposure due to its many industrial uses, and its potential for conversion to the carcinogen N-nitrosodiethanolamine. Dermal application was chosen as the route of exposure to mimic a principal means of human exposure to TEA and because considerable systemic exposure is achieved within this route. Male and female F344/N rats received TEA (purity 98% or greater) by dermal application for 2 years. Under the conditions of these dermal studies, there was equivocal evidence of carcinogenic activity of TEA in male F344/N rates based on a marginal increase in the incidence of renal tubule cell adenoma. There was no evidence of carcinogenic activity in female F344/N rats receiving 63, 125, or 250 mg TEA per kilogram body weight (18).

2-amino-2-methyl-1-propanol AMP (CAS 124-68-5) is of low acute toxicity. The undiluted substance causes corrosion of the eyes and severe skin irritation.

Benzotriazole (BTA) belongs to a class of high production volume chemicals which are added as corrosion inhibitors and biocides in metalworking fluid formulations. In addition, BTA is a commonly employed biocide in metalworking fluids, where it imparts significant microbial toxicity and is resistant to microbial degradation (25).

CONCLUSION

The most frequently occurred compounds of the biocides from the review of 209 MSDS of MWFs are MBO and IPBC followed by the MBM, BHT and 1,6-dihydroxy-2,5-dioxahexane. Total occurrence of substances belong to the formaldehyde releasers present 45 %. The most occurred substances identified as corrosion inhibitors or neutralizing agents are the boric acid, MEA and TEA. Occurrence of DEA is relatively low, representing only 5%.

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