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HUMAN HEALTH CONCENRS OF METALWORKING FLUID COMPONENTS
(Part I – Base oils)

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Abstract

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 widely 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 base fluids in straight oils and their possible health effects.

Key words

Metalworking Fluids, Composition, Base oils, Mineral oil, Health effects

INTRODUCTION

In various manufacturing processes, MWFs are applied to ensure workpiece quality, to reduce tool wear, and to improve process productivity (1). MWFs should have the following characteristics to perform properly: good lubrication, anti-adhesion and wetting properties, good cooling action, high stability, low viscosity, good wetting properties, corrosion inhibition, non-toxic and non-flammable, economical in use and disposal (2). Specific chemical composition of an applied MWF should be strongly dependent on the scope of application. Even small changes of the MWF composition can influence the performance of MWFs in manufacturing processes considerably. Besides defined variations of the composition, the MWF-chemistry furthermore changes over the service life of the fluid (1). Entire life cycle of MWFs includes the manufacture, use on the machine and subsequent disposal of exhausted fluids. As apparent from the following text, the various aspects in the selection of the MWFs, its use and subsequent disposal, e.g. quality aspects, economic aspects, safety and environmental aspects are related together.

Selection, use and disposal of Metalworking fluids

In the process of the selection the right MWF, the aspects of quality play the major role in the decision-making process in particular. For particular machining operation, a properly chosen MWF must ensure particularly good cooling for the machine, and lubricating effect must protect the machined surface against corrosion, while flushing away the chips from the incision site. Care is taken of the workpiece surface quality. Since businesses must be competitive in the market, when choosing the right MWF, economic aspects also play a very important role. Since according to several literary sources such as (3-5), the costs related to using MWFs, may achieve about 15 % of the total cost. It is very important to monitor the ratio of price and the declared lifetime of the MWF and, of course, the costs for the disposal of the fluid. In terms of safety and protection of workers, there are some safety aspects of the selection of MWFs. Currently, MWFs are subject to the REACH regulation; the presence of hazardous substances is thus subject to the strict legislation. When choosing MWFs, especially low dermal toxicity and low respiratory irritation are relevant. Finally, to improve the company's competitiveness and participation in voluntary environmental schemes, the enterprise may take into account the environmental aspects of the used MWFs. From this perspective, the tightening legislation specifies a global trend to reduce the use of metalworking fluids, which still contains a low degradable (and toxic) mineral oil. On the other hand, this trend affects the increasing demands for the fluids declaring good degradability and low toxicity. The environmental aspects comprise the fluid life, tool life and possible environmental disposal methods. When applying MWF to the machine, easy maintenance ensuring the right quality of the fluid plays an important role. To prolong the life of the MWF, it is necessary to do the proper monitoring of selected parameters. Overall, extension of MWFs' life results in saving the resources from the point of premature change of the tools and reduction of the amount of the hazardous waste generated when the MWFs come to the end of their life, while the quality of the machined surfaces still remains at the desired level. In disposing, especially economic aspects and the low cost of disposing methods play the major role. A proper volume reduction at the site may help reduce the cost of waste disposal.

Occupational exposures to MWFs

Occupational exposures to MWFs may cause a variety of health risks. Respiratory conditions include hypersensitivity pneumonitis (HP), chronic bronchitis, impaired lung function, and asthma. Work-related asthma (WRA) is one of the current most prevalent occupational disorders, imposing significant costs of healthcare and workers' compensation. Dermatologic exposures are most commonly associated with, but not limited to, allergic and irritant dermatitis (skin rash) (6). Exposure to MWFs has been associated with increased cancer risk for several cancer sites, including cancers of the bladder, larynx, lung, prostate, pancreas, rectum, and skin (7). Identifying sources of increased exposure is a vital step in hazard identification and control. Studies of MWF aerosol exposure levels in the automobile industry have identified differences in airborne MWF concentrations among different MWF classes, types of machine tools and local exhaust systems (8).

Emission scenario document on the use of MWFs by OECD identified the following releases and exposures to chemicals during the use of MWFs (9):

- Releases from transport container residue (via container cleaning or direct disposal of empty containers); releases from dragout of MWF coating metal parts; releases from filter media disposal and other recycling wastes; or releases from spent MWF disposal;
- Dermal exposures to liquids during transport container unloading or container cleaning; dermal exposures to liquids during mixing and transfer of diluted MWF; dermal exposures to liquids during filtering and other recycling operations; dermal exposures to liquids during transfer of spent MWF and cleaning of machine and trough; dermal exposures to liquids during on-site waste treatment operations and dermal exposure from rinsing, wiping, and/or transferring the shaped part;
- Inhalation exposure from mists generated during metal shaping operations.

Workers in machining environments are exposed to numerous substances and conditions that may affect their health and safety. These exposures are related to chemical, physical, biological, and ergonomic hazards. Occupational safety and health specialists, e.g., industrial hygienists, are trained to prevent, recognize, evaluate, and control inimical exposures in the workplace. Traditionally, a hierarchy of controls is used to protect workers (10). 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. The complexity of the MWFs themselves and the various operations in which they are used makes it difficult to differentiate the type and abundance of specific MWF components, not only within a specific fluid but also among the four fluid types (11). The hazards of any substance can be generally considered as a product of its inherent toxicity and the exposure or dose that a worker receives. More subtle issues may enhance the hazard, such as individual susceptibility to a specific agent or illness (12). Because of adverse effects on human health of some substances, the issue of additives has changed during the decades.

Metalworking fluids composition

Metalworking fluids used in metal shaping operations can be separated into four main groups: straight oils (usually did not contain any water), and water based fluids, such as conventional soluble oils (emulsions) or micro-emulsion (semi-synthetic fluids), and synthetic fluids (usually did not contain any mineral oil). Main advantages and disadvantages of these different kinds of MWFs are listed in Table 1.

All liquid lubricants are formulated with one or more base fluids (mineral based oils, vegetable based oils, synthetic base oils) as the major component, while many additives are added to obtain the optimum properties of the final fluid (9). Many additives are added to the final formulation to ensure specific properties of MWFs, and so commercial products have usually a very complex composition with many components such as biocides, anti-foaming agents, corrosion inhibitors, preservatives, emulsifiers, lubricity improvers and EP-additives, while many of hundreds of combinations may occur (2, 9).

Base oils

The majority of lubricant base fluids are produced by refining crude oil (13). The major negative effect on the environment is particularly linked to its inappropriate use, which results in the surface water and groundwater contamination, air pollution, soil contamination, and consequently, the agricultural product and food contamination (14). If these materials escape to the environment, the impacts tend to be cumulative and consequently harmful to plant, fish, and wildlife (15). Mineral oils are toxic for mammals, fish and bacteria (16). As an alternative to mineral based lubricants, several major categories of synthetic lubricants are available, including synthesized hydrocarbons; synthetic esters; phosphate esters; polyglycols; and silicones. Polyalpha olefins are synthetic hydrocarbons which provide an attractive option for biodegradable lubricants to water, especially for low temperature applications (17).

Table 1 Advantages and disadvantage of different kinds of MWFs (9, 15, 18-24)

MWF	Advantages	Disadvantages
Straight oils	• excellent lubricity • they are relatively easy to maintain • bacterial activity is minimal • once the useful life of the straight-oil MWF is over, the used product can be burned for fuel value or recycled	• low cooling properties • high fire hazards • create mists or smoke • limited to low speed and heavy cutting operations
Emulsions	• great reduction of heat because of water's excellent cooling properties • economy resulting from dilution with water, • better operator acceptance and improved health and safety benefits	• they are prone to intensive microbial deterioration • evaporation losses • rust control problems • softening of hard water may be required (salts react with the emulsifier in the soluble oil to form an insoluble scum which floats on the surface)
Semi-synthetics	• have better lubricating properties than do synthetics • good cooling properties • good microbial control • better rust and rancidity control than emulsions	• foam easily • softening of hard water may be required • stability is affected by the water hardness • easily contaminable by the tramp oil
Synthetics	• excellent cooling properties, non-flammable • good lubricity, longer service life • more environmental friendly then soluble oils • easiest MWFs to maintain • more resistant to biological attack than soluble oils.	• higher the initial cost • poor lubricity • easily contaminable by the tramp oil

A typical composition and the component percentage for different types of MWFs are listed in Table 2.

Synthetic esters are the most interesting alternative to traditional base fluids because of their high quality, possibility to achieve tailor-made properties, no toxicity, and excellent biodegradation. Synthetic esters could provide both the performance level needed and composition to satisfy the environmental aspects demanded of future lubricants (27). While polyalkylene glycols are biodegradable, their degradation rates are slow, relative to those of fatty acids, phosphate esters, and many commonly used surfactants. This bioresistance leads to easier fluid maintenance and longer sump life, and thus lower raw material and disposal costs. Polyalkylene glycols exhibit low toxicity (21). Silicone oils are chemically inert, nontoxic and fire-resistant. They also have low pour points and volatility, good low-temperature fluidity, and good oxidation and thermal stability at high temperatures (15, 27). Vegetable products as well as modified vegetable oil esters can be used as a base stock for preparation of environmentally friendly, rapidly biodegradable lubricants. They are one of possible candidates to replace mineral-based products, because they are almost entirely biodegradable (over 90% biodegradable), nontoxic and well compatible with the minimum lubrication technology.

Vegetable oils are preferred to synthetic fluids because they are renewable resources and cheaper (15, 28-31).

During the review of 85 straight oils MSDS, 10 different compounds of the mineral oil were identified. These 10 substances occurred 55 times in total. CAS numbers, occurrence, CLP or REACH characterization and the concentration in the concentrate are listed in Table 3.

Table 2 Composition of different types of MWFs in % (9, 25, 26)

Type of Additive	Straight oil	Emulsions	Semisynthetic	Synthetic
Mineral oil	60-100	30 - 85	5-30	0
Synthetic lube			40	40-80
Lubricity/ oiliness agents	< 40	< 10	< 20	< 10
EP-additives	< 40	< 20	< 20	< 10
Emulsifiers	0	5-20	5-10	5-10
Corrosion inhibitors	<10	3-10	10-20	10-20
Coupling agents		1-3	1-3	1-3
Biocides		< 2	< 2	< 2
Dyes	0	0-500ppm	0-500ppm	0-500ppm
Anti-foaming agents	0-500ppm	0-500ppm	0-500ppm	0-500ppm

Table 3 Products of mineral oil

	CAS number	Occurrence [%]	CLP/ REACH	Concentration in the concentrate [%]
Distillates (petroleum):				
solvent-dewaxed heavy paraffinic	64742-65-0	22	(*)	10 - 95
hydrotreated light paraffinic	64742-55-8	13	(*)	1 - 50
hydrotreated heavy paraffinic	64742-54-7	18	(*)	5 - 90
hydrotreated middle	64742-46-7	16	(+)	50 - 100
hydrotreated heavy naphthenic	64742-52-5	2	(*)	60
solvent-refined light paraffinic	64741-89-5	7	(*)	10 - 100
hydrodesulfurized middle	64742-80-9	5	(+)	10 - 100
hydrotreated light	64742-47-8	5	(**)	10 - 90
Naphtha (petroleum), hydrotreated heavy	64742-48-9	5	(-)	50 - 100
Paraffin oils (petroleum), catalytic dewaxed light	64742-71-8	5	(*)	40 - 100

Note (https://echa.europa.eu/search-for-chemicals):
(*) According to the harmonized classification and labelling (CLP00) approved by the European Union, this substance may cause cancer. Additionally, the classification provided by companies to ECHA in REACH

registrations identifies that this substance may be fatal if swallowed and enters airways, causes damage to organs through prolonged or repeated exposure and is suspected of damaging fertility or the unborn child.

(+) According to the harmonized classification and labelling (CLP00) approved by the European Union, this substance may cause cancer. Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance may be fatal if swallowed and enters airways, is toxic to aquatic life with long lasting effects, is harmful if inhaled, is a flammable liquid and vapour, may cause damage to organs through prolonged or repeated exposure and causes skin irritation.

(-) According to the harmonized classification and labelling (ATP01) approved by the European Union, this substance may be fatal if swallowed and enters airways, may cause genetic defects and may cause cancer. Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance is toxic to aquatic life with long lasting effects, is an extremely flammable liquid and vapour, is suspected of damaging fertility or the unborn child, causes skin irritation and may cause drowsiness or dizziness.

(**) According to the harmonized classification and labelling (CLP00) approved by the European Union, this substance may be fatal if swallowed and enters airways. Additionally, the classification provided by companies to ECHA in REACH registrations identifies that this substance is toxic to aquatic life with long lasting effects, is a flammable liquid and vapor, causes skin irritation and may cause drowsiness or dizziness.

Mineral oils are distillation products of petroleum, consisting mainly of alkanes (paraffinic oils, P) and/or cycloalkanes (naphthenic oils, N). After refining, the purification can include an acid treatment (oleum method) or catalytic hydrogenation. Linear paraffinic oil has a general alkane structure (C_nH_{2n+2}), but cyclic, branched and alkylated oils have naturally different compositions. Mineral oils can be further classified according to their viscosity (32). Mineral base oils may have carcinogenic properties that appear to be related to their polyaromatic compounds (PAC) content. Severe refining processes remove or substantially reduce the amount of PAC, and eliminate or reduce the carcinogenic activity of mineral base oils. In terms of carcinogenic classification, the European Union has divided mineral base oils into three groups, based on the severity of the refining process: unrefined or mildly refined base oils, highly refined base oils, and other lubricant base oils. Unrefined or mildly refined base oils are classified in category 1A: the substances known to have carcinogenic potential to humans (‘CLP’ Regulation). Highly refined base oils do not have a classification in any of the carcinogenic categories in the European Union. The group of the other lubricant base oils contains a large number of individual CAS numbers with unspecified refining severity. Oils with a Dimethyl sulfoxide (DMSO) extractable fraction equal to or greater than 3% by weight are classified in category 1B: the substances presumed to have carcinogenic potential for humans. Oils with less than 3% by weight DMSO extractable material are not classified in the European Union (‘CLP’ Regulation) (33).

CONCLUSION

The utilization of mineral oil products in all type of metalworking fluids significantly decreased in last few years, while only three MWFs other than straight oils contained the products listed in Table 3. Yet there are lots of machining operations that need only straight oil. The most important information is that, according to CLP, 95% of the listed products may cause cancer.

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