



Metalworking fluids—Mechanisms and performance

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ABSTRACT

In various manufacturing processes, metalworking fluids (MWFs) are applied to ensure workpiece quality, to reduce tool wear, and to improve process productivity. The 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. This paper presents the current state of the art regarding the assumed working mechanisms of MWFs including the effects of desired and undesired changes of the MWF properties.

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1. Introduction

Metalworking fluids (MWFs) have been addressed in several CIRP Keynote Papers in the past as they play a significant role in manufacturing processes such as forming [12], cutting [268], and grinding [27]. They influence heat generation in metalworking processes by reducing friction between tool and workpiece. Cooling is furthermore achieved by dissipating and conducting the generated heat. By their lubricating and cooling properties, MWFs contribute to the avoidance of thermal damage of the workpiece material and reduce wear of the tool [28]. They are of high relevance for the generation [29,100] and understanding [129] of the surface integrity in metalworking. In machining processes chip transportation out of the working zone is a further important subtask of MWFs. The research focus up to now has mainly been on phenomenological studies looking at the improvement of the performance of certain manufacturing processes by MWFs. Less effort was made to clarify their mechanism of action. However, the aforementioned research builds the ideal basis for a cross-process discussion of the shared working mechanisms and the potential regarding knowledge-based improvements of the performance of MWFs.

Bay et al. addressed environmental aspects of lubricants in forming processes including approaches to substitute the MWF by applying special coatings or structured workpiece and tool surfaces [12]. The authors give an excellent overview regarding the potential of oil-based MWFs and emulsions to increase productivity of different forming processes. Although models for the lubrication effect of emulsions are briefly presented, the chemical working mechanisms and the specific impact of varied MWF compositions on the process performance remained untouched.

For cutting processes, a comprehensive summary of the potential to reduce MWF-consumption (for economic and

environmental reasons) is given in the 2004 CIRP Keynote Paper by Weinert and colleagues, who present a definition of minimum quantity cooling and/or lubrication (MQL) approaches as well as scopes regarding the fields of application of both dry machining and MQL [268]. Comparisons between the achievable tool life were made and the requirements regarding tool materials and coatings were derived.

Brinksmeier et al. [27] focused on the avoidance of thermal workpiece damage in grinding processes. Different common concepts of grinding fluids (chemical composition), the state of the art of MWF-supply (nozzles, nozzle positioning, and fluid dynamics) as well as comparative results from grinding experiments revealed the potential of MWFs to decrease the workpiece temperature during machining.

Less focus has been given to the chemical interactions of the surface of the workpiece material and the MWF. Consequently, this paper aims to reveal fundamentals of MWF-chemistry and the presentation of theories on their working mechanisms. Furthermore, a systematic overview on today's possible scenarios for future MWF-concepts are given.

For this purpose, this paper defines metalworking fluids as liquids, which are supplied to a manufacturing process in a way that allows for increased productivity based on lubricating and cooling effects. As general aspects of the fluids are discussed, which are mainly independent from the manufacturing process, commonly used terms such as coolant, lubricant, grinding oil, cutting fluid are summarized as MWFs.

Liquids which are included in the term MWFs have been classified based on different criteria like formulation (oil-based, water-based), manufacturing process (cutting fluid, grinding oil, forming oil, etc.), or quantity (flooding, MQL, etc.). Not all of these classifications are suitable to discuss MWFs and their properties from a mechanism-oriented point of view. According to DIN 51385, MWFs are classified following their composition as oil-based or water-based MWFs [59]. Specific properties are achieved by

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adding specific chemical substances (additives). Fig. 1 shows the classification of MWFs according to DIN 51385 and includes some typical classes of additives, which will be addressed in more detail in Section 1.1 of this paper.

The lipophilic part of oil-based MWF may consist of natural, synthetic, and/or mineral oil: vegetable synthetic, naphthenic, paraffinic, or petroleum oil [11,138] (cf. Section 4.2). MWF-emulsions are stabilized to an oil-in-water (O/W) emulsion by an emulsifier system (often also referred to as surfactants or tensides). Emulsifier-molecules feature a hydrophilic and a lipophilic part. The ambivalent molecules enclose the oil drops and the hydrophilic end of the emulsifier interacts with the water-phase.

Water-based MWFs are purchased as oil-based concentrates, which are dispersed with water at the place of use. Common dilution levels are concentrations of 3–10% of the MWF-concentrate in water [36]. The droplets formed by emulsifiers (cf. Fig. 2) are called micelles. The oily phase inside the micelles includes all lipophilic additives.

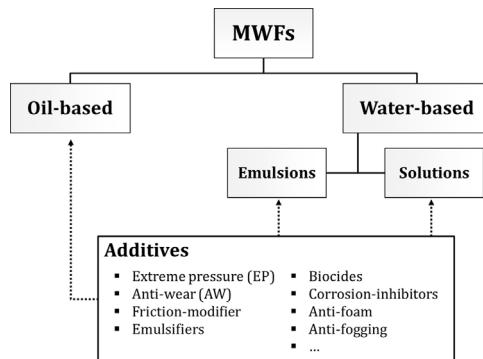


Fig. 1. Classification of the MWF types according to DIN 51385 (simplified) [59,259].

Due to the lack of lipophilic parts, water-based solutions are free of emulsifiers. In solutions, the water is additivated with active polar hydrophilic substances. In Table 1, a comparison of a typical, general formulation of a solution, an emulsion and an oil-based MWF is given.

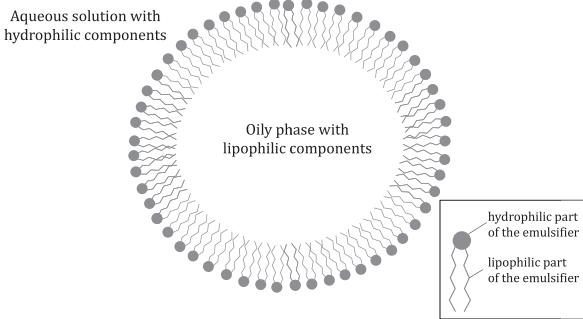


Fig. 2. A micelle of an oil-in-water-emulsion, according to [17,82].

Table 1
Examples of formulations of MWFs of different types [36,207].

Component	Amount (wt %)		
	Solution	Emulsion (5%)	Oil-based MWF
Mineral oil	–	3.5–4.0	75–100
Emulsifiers	–	0.5–1.0	–
Coupling agents	–	0.05–0.25	–
pH buffer	5	–	–
Corrosion inhibitors	10	0.25–0.50	0–5
Extreme-pressure additives	4	0–0.5	5–20
Biocides	2	Unknown	–
Antioxidants	–	–	0–2
Boundary lubricity additives	9	–	0–10
Water	70	95	–

The performance of a certain MWF is influenced by factors such as the type of manufacturing process, the working material, and the tool. Oil-based MWFs e.g. are especially used in processes which require efficient lubrication whereas water-based MWFs are applied when the dissipation of heat is more important than lubrication. However, besides some general approaches for specific manufacturing tasks (cf. Section 3.1), the choice of the most efficient MWF today still is experience-driven in most cases.

The parameters influencing the performance of MWFs are summarized in Fig. 3 including the sections of this paper, which cover the relevant fields of this complex topic.

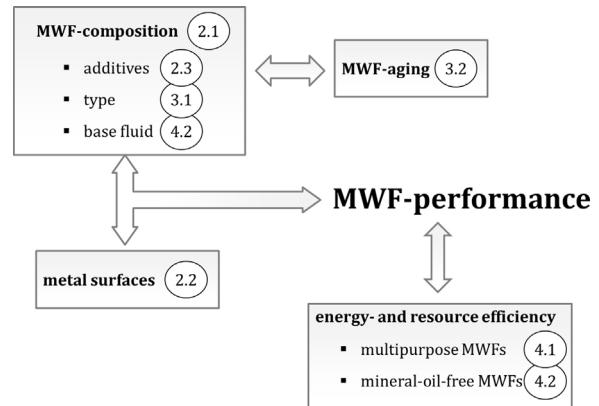


Fig. 3. Parameters influencing the performance of MWFs. Encircled: sections of this paper, addressing the corresponding parameters.

1.1. History and demand for MWFs in manufacturing technology

Early approaches for the support of metalworking processes by fluids utilize two basic properties of liquids: their ability to dissipate heat and to reduce friction by lubrication. Leonardo da Vinci created several test set-ups allowing for the analysis of friction under varied conditions (Fig. 4). Beside of the use of pure fats and oils, early MWFs were mixtures of water (which has the highest heat transfer coefficient) and additional substances for the improvement of the MWFs' properties, especially the lubrication ability.

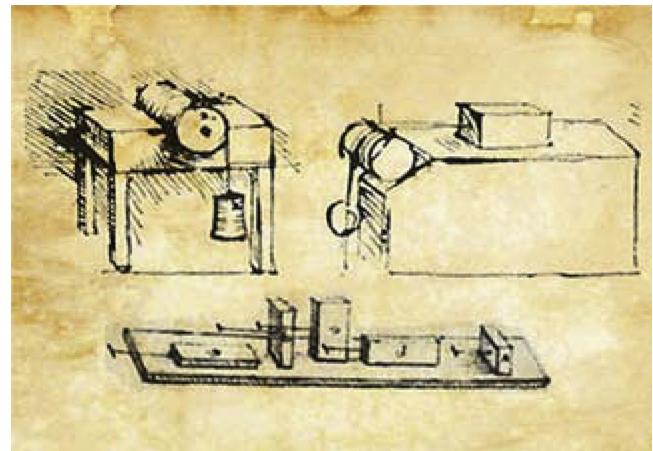


Fig. 4. Leonardo da Vinci's sketches of tribological test set-ups for the analysis of friction [154].

Natural products such as animal oils and fats (primarily whale oil, tallow, and lard) as well as vegetable oils from various sources such as olive, palm, castor, oil plant and other seed oils were used to compose the first MWFs. They were applied in manufacturing processes e.g. for the production of metal artwork and weapons in the middle age [36,62]. In further work of da Vinci, a mixture of oil and corundum was applied for lubrication purposes in an internal cylindrical grinding machine. Special grooves were inserted to the grinding wheel to allow for efficient supply of the MWF to the tool [284].

In the early 19th century, the design of machine tools made considerable progress and simultaneously, the techniques for the

supply of MWFs were improved [284]. In his autobiography [162] James Nasmyth describes his inventions, e.g. a traversing drill, which had a small tank to supply water or soap in water ("as a lubricator") directly to the contact zone. The increased availability of mineral oil around 1850 had an intense influence on the composition of MWFs. The oil, which was a by-product of refining kerosene, was chosen to replace animal and vegetable oils in MWFs due to its low price [62].

At the end of the 19th century, the first systematic publications addressed the lubricating effect of MWFs by means of the ability to reduce the friction between tool and workpiece. Furthermore, specific approaches regarding the supply and re-application (filtration) of MWF were presented [134,245]. In 1906, Taylor published his investigations aiming on an increase of the performance and productivity of the Midvale steel company (Philadelphia, USA) in his book "On the art of cutting metals" [242]. He succeeded in achieving higher production rates in metal cutting by optimizing cutting speeds and feed rates. Precondition for this development which lead to an increase of chip removal rates of up to 40% was the supply of a constant stream of water to the point of the tool engagement. He also established a first "coolant circulation system". The MWF called "suds"—consisted of water which was saturated with sodium carbonate to prevent corrosion [36,242].

With the progress of industrialization in the 20th century, there was an increasing need for MWFs with higher performance. It was found that the addition of substances containing sulphur and phosphorus lead to improved lubricating ability of the applied MWFs. The sectors of aviation and automotive industry were the main drivers of these developments focusing on higher levels of productivity in mass production (cf. Fig. 5) [229]. "Trial & error" was a base principle for the development of new MWFs with improved functionality.

In the middle of the 20th century, the use of water-based MWFs gained more and more importance. Oil-in-water-emulsions consist of an organic part, which contain lubricating substances, and water. Thereby, emulsions represent the first specific approach to combine cooling and lubricating within one MWF. The combination of hydrophilic and lipophilic substances in one liquid phase requires the application of stabilizing substances: emulsifiers. The selection of emulsifying components was strongly related to the scientific research and publications regarding some fundamental theories: the surface tension theory, the adsorption film theory, the hydration theory and the molecular orientation theory by Langmuir [120], Harkins [83] and Mulliken [152] (cf. Section 2.1). The performance of oil-based MWFs was improved by adding further additives which contained sulphur, phosphorus, chlorine, or boron. It was found that these substances are suitable to increase the lubricating ability under high pressure and furthermore prevent corrosion [217,229].

The demand for high performance MWFs led to the identification and application of further additive classes, resulting in highly complex fluids with more than 300 different substances. Within the last few decades regulations with regard to environmental protection and occupational health have restricted the use of certain chemical substances.

Guidelines such as the "Globally Harmonized System of Classification and Labeling of Chemicals" (GHS) [58], "Registration, Evaluation, Authorisation and Restriction of Chemicals" (Reach) [16], and "Environment, Health and Safety (EHS)" assessments [224], limited e.g. the permitted concentrations of volatile organic compounds (VOC) [78,147], and biocides such as formaldehyde-emitting substances [71]. Today, MWF-producers have to face a large number of guidelines and legal requirements, which influence the development of MWFs [135]. However, modern water-based MWFs still contain between 15 and 60 different chemical substances [84,157].

Despite the indisputable demand to fulfill the adapted requirements of the MWF-composition for the sake of the operators' health, the changes given by regulations were without any doubt

accompanied by considerable drawbacks from a technological point of view. Boric acid, amines and chlorinated products were well established components of MWFs and are no longer allowed to be used in the products as they are suspected to cause health issues such as cancers of the skin, scrotum, larynx, rectum pancreas, and bladder [71,156]. Already in the 1980s, the carcinogenic effects for N-nitrosamines [155] (cf. Section 3.2) and some polycyclic aromatic hydrocarbons (PAH) [96] were verified in animal experiments. Furthermore, the specific combination of substances applied by that time was found to be the potential cause for chronic dermatological diseases. According to the German ordinance on occupational diseases, 23% of patients with toxic, toxic-degenerative and allergic contact eczema frequently got in contact with MWFs [7,9].

Driver	Effect on MWF-composition
	Demand to machine metals Development of first MWFs based on natural products e.g. water, animal or vegetable oils
	Industrialization (machine tools) Availability of mineral oil Replacement of natural MWF-components First investigations on the lubrication ability of the used MWFs
	Superior tool and workpiece material Advanced machine tools Mass-production Addition of numerous chemical substances to increase the technical performance Application of chlorinated MWFs containing boric acid and further harmful chemicals First approaches to reduce amount of mineral oil in MWFs (driven by the rising oil-price)
	Regulation Energy- and resource efficiency Substitution or elimination of chlorine and further harmful substances Assessment of the sustainability of MWFs Interdisciplinary assessment of MWFs

Fig. 5. Chronology development of MWFs according to [229,242,271,284].

In addition to legal compliance the availability and cost for the basic fluid as well as the additives are of importance. Still today, the majority of oil-based MWFs as well as the lubricating parts of water-based MWFs are derived from mineral oil (cf. Section 4.2 of this paper). Between 1970 and 2014, the price of crude oil increased by the factor of 20 (see Fig. 6) [158].

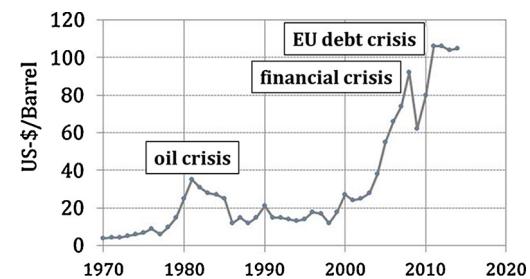


Fig. 6. Price development of the crude oil: US-\$/Barrel [158].

Comparable price situations are obtained for several additives in oil-based and water-based MWFs. As a consequence and for environmental and economic reasons, the MWF-producing industry is continuously looking for new mineral oil free raw materials which fulfill both, legal specifications and technological requirements (cf. Section 4.2). The large variety of today's MWFs and MWF-application concepts (e.g. MQL) is a result of an iteration process to meet the specific demands of manufacturing processes. Starting e.g. with water to achieve an efficient dissipation of heat,

the demand for corrosion inhibitors was inevitable to protect workpieces and the machine tool. In an environment with water and corrosion inhibitors, a microbial growth is likely so biocides had to be added. To improve lubrication, the addition of lipids leads to the demand of emulsifiers. As especially emulsifiers may cause foam formation during a manufacturing process, anti-foam additives became necessary. This short example of an iteration process for the development of a basic water-based MWF promptly lead to a complex mixture of MWF-components (water, lipids, corrosion inhibitors, biocides, emulsifiers, anti-foam additives).

Functionality and stability of MWFs are ensured by a number of additives such as surface active additives (EP (extreme-pressure) additives, AW (anti-wear) additives, etc.), corrosion inhibitors, biocides, and emulsifier [228]. Emulsifiers, biocides and corrosion inhibitors are especially for water-based MWFs, whereas surface active additives and stabilizing substances are applied in all MWFs. The most common additives are summarized in [Table 2](#).

Table 2

Compilation of additives used in MWF during the last decades, associated examples and their function according to [11,64,109,138,217,228].

Additive type	Substances	Mode of action, function
Anti-aging-additive, oxidation inhibitor	Aromatic amines, Organic sulphide, zinc dialkyldithiophosphate	Prevention of oxidation of base oil at high temperatures and stabilization
Anti-wear-additive, AW	Acid and nonionic Phosphoric acid ester, zinc dialkyldithio-phosphate,	Reduces abrasive wear of rubbing surfaces by physisorption
Biocides	Phenol derivatives, formaldehyde releasers, isothiazolinones	Prevention of excessive microbial growth (cf. Section 3.2)
Detergent, dispersant	Sulfonate, phenolate, salicylate	Prevents build-up of varnishes on surfaces, and agglomeration of particles to form solid deposits, promotes their suspension
Emulsifier	Anionic: sulfonates, potassium-soap, alkanolamine-soap; Nonionic: fatty alcohol ethoxylate, fatty acid amide; Cationic: quaternary ammonium salts	Emulsion formation and stabilization
Extreme-pressure-additive, EP	Chlorineparaffine, sulphurous ester, phosphoric acid ester, polysulphide, PS	Protection against wear by formation of adsorption or reaction layers, prevent microfusing of metallic surfaces
Foam inhibitor	Silicone polymers, tributylphosphate	Destabilize foam in oil
Friction modifier, FM	Glycerol mono oleate, whale oil, natural fats, oils, synthetic ester	Lowers friction and wear, improve adhesion of lubricating film
Metal-deactivators	Heterocycles, di-amine, triaryl phosphite	Adsorptive film formation
Passive extreme-pressure-additive, PEP	Overbased sodium or calcium sulfonate	Kind of solid lubricant, surface separation by film formation (cf. Section 2.3)
Corrosion-inhibitor	Sulfonate, organic boron compounds, amine, aminophosphate, zinc dialkyldithiophosphate, tall oil fatty acids	Limits rust and corrosion of ferrous and non-ferrous metals (prevention of oxidation)
Viscosity index improver, VI	Polymers	Increases viscosity index of the lubricant (cf. Section 2.1)

Further modifications of the MWF-composition result from the specific characteristics of the applied manufacturing process accompanied by the requirement to meet the current legal regulations. Thus, it is likely that the future of MWFs (composition and application) will not lead to a unique holistic approach. Nevertheless, there are some process-independent working mechanisms that make MWFs a mandatory tool in many areas of manufacturing.

1.2. MWF-supply concepts

Besides the different types of MWFs, substantial research has been performed focusing on the way how to apply the MWFs in a most appropriate way. In general, the application-strategies can be subdivided into

- flooding,
- minimum quantity lubrication (MQL),
- cryogenic cooling,
- simultaneous use of MQL and cryogenic cooling, and
- solid lubrication.

These approaches are known to play a relevant role in manufacturing processes regarding economic and environmental aspects [36,101,102,269].

Recent research on MWF-flooding aims at the energy efficient supply of the MWF [1,54,85,170], the increase of productivity [191,192,269] and the comparison of different MWF-compositions [225,240,241,279]. A lot of effort is performed especially for abrasive machining processes, as these are very demanding regarding a reduction of friction-related heat or the cooling of the contact zone respectively. In a conventional grinding process, specific flow rates of approximately 2–4 l/min mm are common [264].

The application of very small amounts of MWF is the target of the MQL-concept (max. 50 ml/h) and minimum quantity cooling lubrication (MQCL, max. 2 l/h) [269]. The MQL-supply is performed using pure oil-based MWFs or oil-based MWF/air mix, whereby the lubricating efficiency is the crucial aspect. The MQL-concept aims on the reduction of friction between tool and workpiece material and the prevention of adhesion of chips on the tool. It is mainly applied in forming [12] and cutting processes [5] but less in abrasive machining processes such as grinding [46,239]. As the low quantity of MWF allows no cooling of the workpiece, the use of the MQL-technique is critical to a large number of manufacturing processes [24,26].

Cryogenic cooling of the contact zone between tool and workpiece is achieved by media such as liquid nitrogen (LN_2 , -196°C) or CO_2 -snow (ca. -50 to -78°C). It is mainly applied in cutting processes [183,222] including difficult-to-machine materials [261] such as Inconel [2] or titanium [18]. Furthermore, it has been applied to improve the surface quality [293] and the wear resistance of diamond tools in precision steel machining [67]. For other purposes such as the generation of an advantageous surface integrity in different materials, cryogenic cooling is also applied in combination with turning [6] and forming processes [40,142,182]. Cryogenic processes will not be discussed in this paper in detail, as a 2016 CIRP Keynote Paper will summarize the state of the art of this cooling concept.

To combine the lubricating effect of MQL and the cooling ability of cryogenic media, there has been some work on simultaneous cryo-MQL-supply [108,132]. In grinding, an increased tool life has been obtained.

Solid lubricants are rarely used, and for very specific applications only. Recent investigations comprise the effect of graphite and boric acid [115], pure graphite [76], calcium fluoride, barium fluoride, molybdenum trioxide [43], and molybdenum disulphide [193] in grinding or hard turning to improve surface finish.

2. Working mechanisms of metalworking fluids

Besides the general functionality of MWFs, which includes the ability to cool and to flush the contact zone between tool and workpiece, decisive effects which improve the performance of MWFs are based on chemical working mechanisms. Even though the use of MWFs has a long tradition, not all of the mostly empirically obtained effects of MWFs are fully understood until today. Furthermore, the model-based theories dealing with potential working mechanisms are still discussed very controversially.

The tribological systems “machining” and “forming” are characterized by the surfaces of a tool and a workpiece that are in moving contact together with an intermediate medium (MWF) which significantly influences the tribological conditions. Fig. 7 gives an overview regarding the tribological system and the relevant physical and chemical aspects addressed in this section.

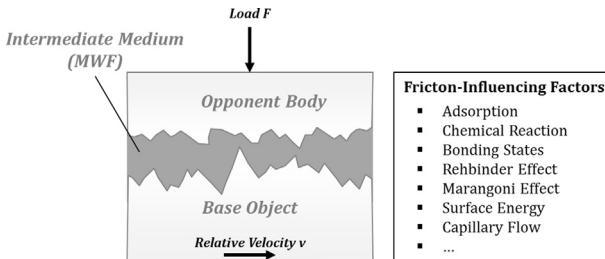


Fig. 7. Tribological system “machining” or “forming” with assumed physical and chemical interactions between the components.

To evaluate the performance of a MWF a system perspective covering the properties of the MWF, the tool and workpiece material as well as the kinematical aspects of the process is required.

2.1. Physical and chemical aspects of MWF-application

The performance of a MWF is the result of a complex combination of chemical and physical effects. In practice, these effects overlay each other, which makes it hard to separate single effects. Nevertheless, the understanding of the individual mechanisms allows for explanation of the observed effects for the majority of the published data.

One decisive factor for the discussion of the working mechanism of MWFs is the type of interaction with the involved metal surfaces. In 1970, Forbes et al. published a theoretical concept regarding the interactions of sulphur-containing additives leading to the formation of layers of inorganic sulphur (not necessarily iron sulphides (FeS)) at metal surfaces [69]. His work is discussed controversially and initiates the scientific analysis of the working mechanisms of surface-active-substances. The result of this discourse is summarized in Fig. 8 indicating the three assumed possible working mechanisms of sulphur-containing additives: physisorption (physical adsorption), chemisorption (chemical adsorption) and chemical reaction [35].

Independently from the type of interaction, metal surfaces and additive molecules can only interact with each other based on close physical proximity. Inter- and intra-molecular interactions are relevant for the ability of additives to improve the MWFs’ functionality. When an additive molecule approaches the metal surface, at a certain point, the minimal distance between the molecule and the surface falls below a critical limit, leading to weak intermolecular interactions: van der Waals forces or van der Waals interaction. These van der Waals forces act only over a small distance (see Table 3).

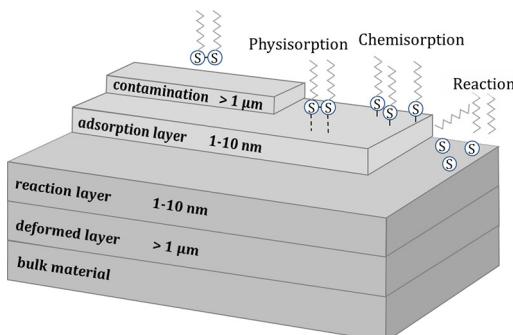


Fig. 8. Schematic sketch of a machined surface including assumed ways of interaction of sulphur-containing additives, according [30,35,69].

In general, the van der Waals forces are divided into three different types depending on the type of dipole (weak polarization of different parts of a molecule) interaction and the arising strength of interaction: Debey-, London-, and Keesom-forces [4,127].

Stronger intermolecular interactions occur when polarized functional groups of molecules with a free electron pair like $-\text{NH}$, $-\text{OH}$, $-\text{F}$ are involved which are able to form hydrogen bonds. The polarization leads to a certain electrical orientation of the molecules and influences their physical behavior.

The high surface tension of water is a well-known and evident example of this effect. Atkins indicates that the hydrogen bonds slightly dominate van der Waals forces regarding the strength of interactions (cf. Table 3) [4]. In the following, the types of interactions of additives with metal surfaces are discussed by looking at effects based on adsorption (physisorption and (in some cases) subsequent chemisorption) or chemical reactions.

Table 3

Overview of intermolecular and intramolecular interactions including the distance dependence as a function of the radius r around the functional group, according to [4] and [31].

Interaction type of forces	Interaction	Distance dependence	bond energy [kJ/mol]
Debey-forces	Dipole-indirect dipole	$\sim 1/r^6$	<2
London dispersion	Indirect dipole-indirect dipole	$\sim 1/r^6$	0.1–40
Keesom-forces	dipole-dipole	$\sim 1/r^3$	<20
Hydrogen bonds	A-H...B with A,B=O,N,S,F		<50
Coulombic-forces	Ion-ion	$\sim 1/r$	600–1000
Atomic bond	Covalent	$\sim 1/r$	60–700

From an energetic point of view, the enthalpy of physisorption is substantially lower than for chemisorption. By adsorption of active molecules at the metal surface, existing bonds (such as a hydrate shell) are broken-up and new interactions among the additive molecules and the atoms at the metal surface take place. In Fig. 9, the potential energy profile for the adsorption of a molecule from a metal surface is given. In this case, physisorption and subsequent dissociative chemisorption are presented. Dissociative chemisorption is characterized by the process of molecular splitting of the

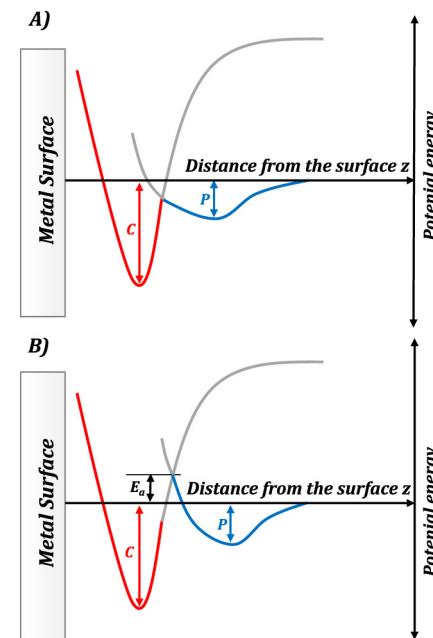


Fig. 9. Potential energy profiles for the physisorption and chemisorption of a Molecule. P is the enthalpy of physisorption and C that for chemisorption (A) without activation energy and (B) with activation energy, simplified according to [4].

approaching additive molecule. In the graphs, a molecule approaches the surface and the energetic level decreases when it is adsorbed into the physisorption state (P).

In case that the potential energy barrier is low, the molecule is directly transferred into the state of chemisorption (C). If the energy barrier is higher, activation energy (E_a) is required to overcome the energetic barrier and to allow for chemisorption. Based on the energy level, chemisorption leads to more intense interactions of the molecules. This can be correlated with the lubricating ability of the additive molecules. Those molecules, which are able to interact via chemisorption, improve the lubrication significantly. As for some cases activation energy has to be induced to allow for chemisorption, the efficiency of the additives is dependent on the surrounding conditions (e.g. machining parameters).

A good example can be found in the results from grinding tests presented by Brinksmeier et al. applying sulphur-containing additives in grinding [28]. Based on these findings, the additives lead to a better lubrication at higher energetic levels of the grinding process (Fig. 10).

At lower equivalent chip thicknesses, the presence of the additive did not lead to positive effects. Especially for lower cutting speeds, the slope of the curves is strongly dependent on the presence of sulphur-containing additives. At low equivalent chip thicknesses, non-additivated MWF leads to the best results, whereas at equivalent chip thicknesses higher than 2.5 μm , the performance of the process was improved by the additives. The threshold is assumed to indicate the process conditions, which allow for overcoming the required activation energy. At this point and at higher energy levels, physisorption and subsequent chemisorption takes place.

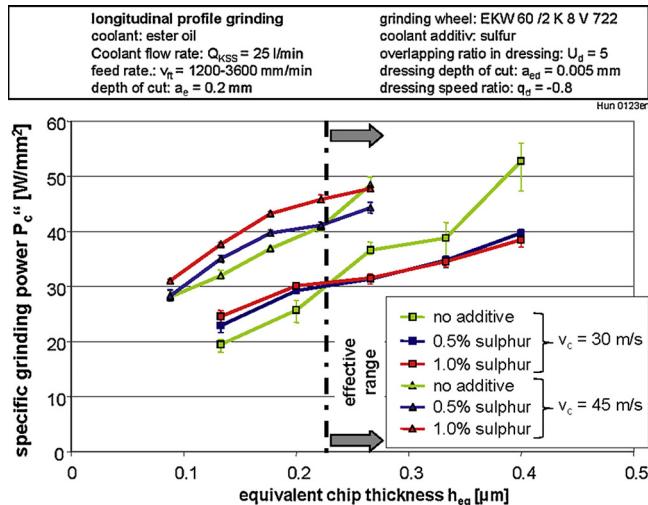


Fig. 10. Specific cutting power P_c'' as a function of equivalent chip thickness in a grinding process revealing an effective range of sulphur additive [28].

Energy-based considerations regarding the ability of sulphur- and phosphor-containing additive molecules with metal surfaces were furthermore presented by Spur and colleagues [230]. The authors revealed that the assumed reactions of sulphur containing additive molecules with Inconel surfaces occur at room temperature whereas higher temperatures are required for reactions of phosphor-containing additive molecules with the metal surface (Fig. 11). However, time-aspects (see below) have been neglected in these considerations.

Physisorption and chemisorption (adsorption) are mandatory mechanisms, which have to occur prior to a subsequent chemical reaction. When the surface material and the approaching molecule (adsorbate) lose their individual electron structures and form an entirely new molecule, with its own properties, a chemical reaction is completed. New intramolecular interactions result from a chemical reaction: covalent atomic bonds. In the schematic illustration of Fig. 8, the sulphur atoms of the additive release

Precondition for a chemical reaction: free energy $\Delta G < 0$

- 1/3 Ni₃Al + S = NiS + 1/3 Al
- △ 1/3 Ni₃Ti + S = NiS + 1/3 Ti
- 1/3 Cr₃C₂ + S = CrS + 2/3 C
- ▲ 1/7 Cr₇C₃ + S = CrS + 3/7 C
- ◆ 1/23 Cr₂₃C₆ + S = CrS + 6/23 C
- 2/3 Ni₃Al + S = 1/3 Al₂S₃ + 2 Ni
- Ni₃Al + P = AlP + 3 Ni
- ◇ Ni₃Ti + P = Ni₃P + Ti
- Ni₃Al + P = Ni₃P + Al
- ▲ 2/5 Ni₃Al + P = 1/5 Ni₆P₅ + 2/5 Al
- ◆ 5/6 Ni₃Ti + P = 1/2 Ni₅P₂ + 5/6 Al
- 5/6 Ni₃Ti + P = 1/2 Ni₅P₂ + 5/6 Ti
- △ 2/5 Ni₃Ti + P = 1/5 Ni₆P₅ + 2/5 Ti

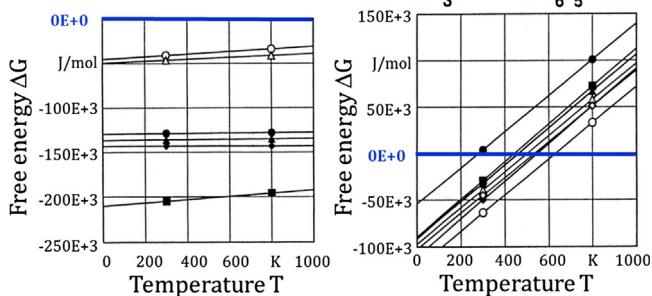


Fig. 11. Gibbs free energy for the reaction of sulphur-(left) and phosphor-containing (right) additives with the surface of Inconel 738 at different temperature levels [230].

their organic groups to the environment and form sulphides (e.g. iron-sulphide) [35]. However, chemical reaction is not a mandatory step, to occur after physisorption and chemisorption. Chemisorption, physisorption and chemical reactions have to be considered regarding their combined occurrence in chemical processes. For example, the formation of oxide layers at metal surfaces, Brucker et al. have proven oxygen chemisorption to be an intermediate step before chemical reaction of the oxygen with α -Fe takes place [33].

The question of the dominating working mechanism of MWFs is closely linked to time aspects. Considering the contact time between tool and workpiece in machining processes such as cutting or grinding, the new surface is generated within a time scale of milliseconds. For some of the assumed chemical reactions, this time slot is not sufficient to allow for the break-up and formation of covalent bonds. Adsorption is a much faster mechanism, which might well be completed in the processing time. The following sections of this paper will reveal that in addition to time-aspects, the place of interaction between MWF, tool and workpiece must be discussed thoroughly. Favorable effects of (additivated) MWFs in manufacturing processes are undeniable (e.g. [51–53,167]). Therefore, working mechanisms which are consistent with the conditions in terms of time and location must be responsible. The identification of the most likely effects is the topic of the following sub-sections:

2.1.1. Rehbinder effect and microcracks

In 1928, the Russian chemist P.A. Rehbinder presented a new theory regarding the influence of polar substances on the surface energy of mineral crystals by forming layers at the interfaces [200]. In several experimental investigations, Rehbinder and colleagues observed a strong reduction of the strength and hardness of these crystals caused by e.g. oleic acid solved in petrolatum oil. Rehbinder explained this effect by "weakening the bonds between the surface elements of a lattice due to the adsorption of surface active molecules" [197]. The place of action was referred to as "microcracks", which result from pre-machining and are discussed to be present in nearly all workpieces of practical relevance. The adsorption of active polar substances and the existence of irregularities like microcracks and/or rearrangement of interatomic bonds in a solid lead to a decrease of the strength also of metal specimens [197,199]. Rehbinder's approach was groundbreaking since until then the chip fracture was referred to the dissociation of bonds in a solid under the action of an external load but without taking into account an influence of chemical aspects [133]. Several in-depth papers were published discussing the potential of the Rehbinder effect for different manufacturing processes [125,133,211,220,221].

The Rehbinder effect implies a relation between the free energy of a surface which is generated in a machining process and the

strength of the solid. In the early 20th century, Griffith investigated "The Phenomena of Rupture and Flow in Solids" (at e.g. metal and glass) and established a quantitative relation in case of cracks:

$$\sigma_s = \text{const} \sqrt{\frac{E_\gamma \gamma_s}{L_c}} \quad (1)$$

where σ_s = ultimate strength (fracture stress), E_γ = Young modulus, γ_s = surface free energy per unit area and L_c = length of an initial surface crack.

The formula describes the dependency of the strength of a material from the surface free energy and crack length. As a consequence of this relation, the reduction of the surface free energy (as it is achieved by adsorption of surface active molecules) leads to a decrease of the strength of the material. A decisive factor in the theory presented by Griffith is the existence of (micro-)cracks at the surface [79,133].

Until today, the occurrence, size and location of microcracks at freshly generated metal surfaces is not really clarified. According to Rehbinder et al. the surface active substances (e.g. valeric acid, stearic acid, etc.) diffuse into microcracks formed at a freshly cut surface and prevent re-welding [198]. Regarding the interactions of additives with surfaces of microcracks, Epifanov proposed that an additive molecule will degrade at an activated (fresh) metal surface [65].

Usui et al. investigated the place of interaction of tetrachloride (CCl_4 , one of the most used additives in MWFs until regulations prohibited the application) with copper surfaces in cutting processes. Here, the application of tetrachloride solely at the back face of the chips caused a reduction of the cutting forces [253]. The effect was held responsible for the prevention of the re-welding of microcracks at the chip surface during the deformation and thus a reduction of the material's strength.

Barlow et al. also explored the Rehbinder effect based on experiments using tetrachloride as a surface active substance. Instead of conventional flooding, they applied tetrachloride on copper in small amounts to generate a thin liquid film on the surface. The fluid was applied on the workpiece surface right in front of the advancing shear zone. In these experiments, the carbon or chlorine of the tetrachloride was replaced by their related isotopes ^{14}C and ^{36}Cl . The authors detected these isotopes at the chip back face after the process. Furthermore, they measured the concentration of the isotopes over the depth below the surface. As they did not obtain any concentration gradients, they concluded that the performed investigations were not able to prove the existence of (not re-welded) microcracks [8].

Publications analyzing the formation of cracks consider the thermodynamics and kinetics of the chemically assisted fractures in materials. The surface active substances are able to reduce the amount of energy required for breaking-up the bonds at the tip of the crack (see Fig. 12). These effects are strongly depending on the solid material used and the surface active substances. Computer simulations of iron as a workpiece material have shown that the tip region of a crack has a relatively open geometry with room for molecules of modest size which are able to diffuse into the cracks [243,244]. These results support the assumption that additives in MWFs facilitate separation of the workpiece material based on the interactions with the metal surface.

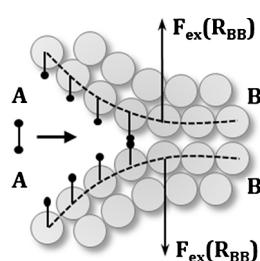


Fig. 12. One-dimensional model of crack propagation according to [133,243].

There are also several publications, which discuss the Rehbinder effect itself as well as its influence on metalworking processes in a more controversial way: Revie points out that "much of the work reported in the literature has not been controlled with sufficient rigor and, for this reason, the Rehbinder effect has a reputation of having poor reproducibility" [186,201]. Also Tostmann classified the Rehbinder effect as a simple strength shift at the surface of metallic materials instead of formation deeper intergranular cracks [250].

Despite some significant findings supporting the discussed types of interactions, based on the published data it has to be stated, that the final evidence to confirm or disprove the relevance of the Rehbinder effect on metalworking fluids has not been published so far. Furthermore, it seems to be clear that a high number of parameters such as temperature, stress within the workpiece material, and the activity of the external medium have an influence on the obtained effect [137].

2.1.2. Surface free energy and surface tension

The so called wettability of MWFs is another aspect to consider as a good wettability seems to indicate a high efficiency of the fluid. An approach to describe the wettability of MWFs at metal surfaces is the analysis of the surface free energy and the surface tension by measuring the contact angle Θ (cf. Fig. 13). The specific surface free energy and surface tension between phases in contact are used to explain wetting processes in the thermodynamic adhesion theory.

Already in 1805, Young realized the relationships between forces and energies at the interfaces of the three different phases: solid, liquid and vapor. He postulated the Young equation [289] which describes the state of equilibrium at the interfaces of phases. Several further comprehensive and fundamental studies [75,285,292,293] have followed up the investigations from Young to describe the system specific surface free energy between the phases and were able to substantiate the equation:

$$\gamma_s - \pi_e = \gamma_{sv} = \gamma_l \cos \Theta + \gamma_{sl} \quad (2)$$

where γ_l = surface tension of the liquid phase, γ_s = surface free energy of the solid phase, γ_{sl} = surface energy at the interface of the solid/liquid phase; γ_{sv} = surface energy at the interface of the liquid/vapour phase; Θ = contact angle and π_e = spreading pressure

Owens & Wendt, Rabel, and Kaelble established a special method to calculate the surface free energy of a solid from the contact angle with liquids. In this method, the surface free energy is divided into a polar part and a disperse part of the liquids so that this method is particularly suitable for the investigations of the

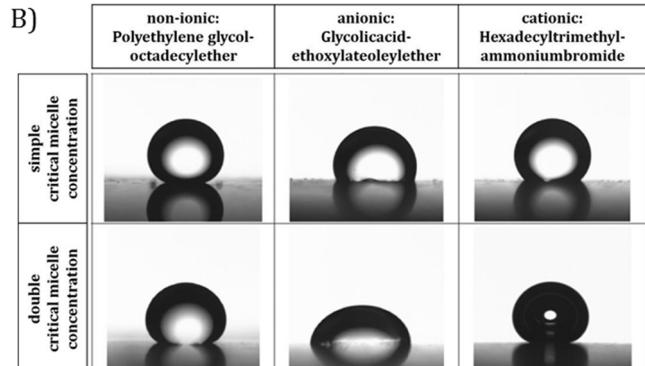
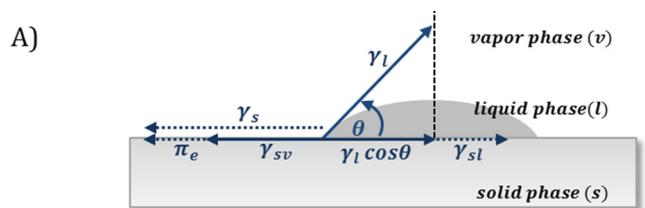


Fig. 13. (a) Calculation of the contact angle Θ of a sessile drop according to [75], (b) contact angle measurement: images of drops (base oil/surfactant/water) on a polished AISI 1015 steel surface [37].

influence of lipophilic and hydrophilic coatings with MWFs [172,184].

Several investigations varying the workpiece material and the composition of MWF were performed to assess the wettability of surfaces by MWFs [130,138]. In Fig. 13(b), results from Cambiella et al. are shown which illustrate the influence of different emulsifiers (cationic, anionic and non-ionic surfactants) on the surface free energy of emulsion drops.

In general, with decreasing contact angle (between liquid and solid phase), the wetting ability is enhanced. In this case, adhesion of chemical substances in the liquid on the solid surface is facilitated [75]. This would allow improved lubrication in metalworking based on interactions between additives and the metal surface [37].

2.1.3. Capillary flow and Marangoni effect

The surface tension has an influence not only on the vapor pressure but also on the capillary flow. Both effects are relevant factors for the ability of surface active substances (additives) in fluids to penetrate (micro-)cracks according to the Rehbinder effect. The capillarity of MWFs was investigated, besides others, by Smith et al. by developing a theoretical model based on capillary flow theory in a cutting process with tetrachloride as surrounding fluid. It is stated that fissures in the chip as well as along the tool-chip interface allow for MWFs or vapor to be transported rapidly into the chip and along the tool-chip interface [226]. Considering time-aspects of manufacturing processes, the quick transportation of MWFs to the relevant places of interaction with the metal surface, is crucial to obtain an effect of MWF-application. The capillary flow significantly supports the transportation process.

The Marangoni effect/convection [136] is a physical interrelation, which describes the behavior of fluids depending on the temperature gradient in the surrounding area [110,257]. This effect is a surface-tension-driven phenomenon, as the surface tension is depending on the temperature ($d\sigma/dT \equiv -\sigma_T < 0$). This leads to thermocapillary fluid flow and instabilities in non-isothermal free surface systems as theoretically illustrated in Fig. 14 [50,256].

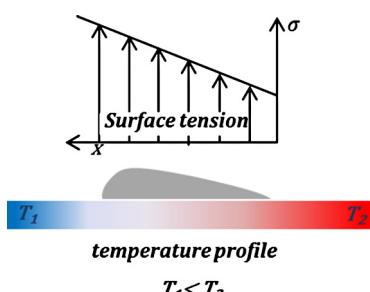


Fig. 14. Schematic illustration of the temperature-dependent surface tension in liquids (here: a drop at a solid surface).

The relevance of the Marangoni effect can be found considering that in metalworking the highest temperatures are found directly at the contact zone between tool and workpiece ([49], cf. Fig. 15). Based on the Marangoni effect, the MWF physically prefers to move away from the zones of highest temperatures.

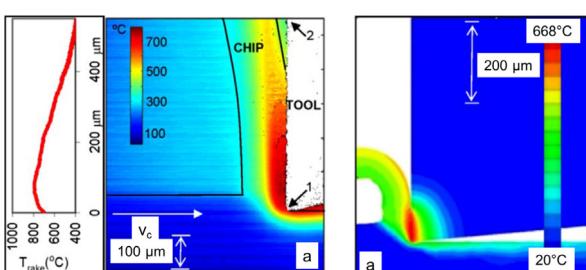


Fig. 15. Temperature distribution within the contact zone in cutting [48].

Dai et al. investigated the influence of the surface roughness and the orientation of grinding marks (parallel and perpendicular) on the thermo-capillary migration of paraffin oil. Grinding marks in parallel to the temperature gradient can be considered as micro-capillaries inducing an extra force $F_{capillary}$.

The Marangoni number (Ma) represents the imbalance caused by the thermocapillary force and is defined by Eq. (3) [19,80] with the reference velocity given in Eq. (4):

$$Ma = \frac{rv_0}{\kappa} \quad (3)$$

$$v_0 = \frac{|\sigma_T||\Delta T_\infty|r}{\mu} \quad (4)$$

where r = radius of the drop, κ = thermal diffusivity, μ = dynamic viscosity, σ = interfacial tension between the drop phase and the continuous phase, v_0 = reference velocity and T = temperature.

In case that the Marangoni effect dominates the capillary force, the liquid would migrate to areas of lower temperature. Considering the temperature distribution of a manufacturing process (as shown for a cutting process in Fig. 15) the assumption of migration of MWF into the contact area seems rather unlikely. For these conditions, the undeniably positive effects of MWF-application must be caused by interactions at other sites of a machining process such as the chip's back face.

2.1.4. Viscosity

The viscosity has to be taken into account in relation to the Rehbinder effect, the surface energy and the Marangoni effect. It is the main factor influencing the capability of oils to maintain a satisfactory lubricating film, but also the oil's ability to flow [227]. Water-based MWFs have a comparably low viscosity. The surface active substances are used in small concentrations (see Table 1), most of them are more lipophilic and thus solved in the oil droplets of a micelle. Therefore, for water-based MWFs, the influence of the viscosity of surface active substances can be neglected. For oil-based MWFs, the high viscosity of additives such as polysulphides is a notable factor. An increase of the concentration of an additive may come along with higher viscosity (and thus better adhesion ability) of the MWF. This makes it hard to trace back an influence of the varied additive concentration. Positive effects may be due to the interaction of the additive with the metal surface but also the improved formation of an adhered liquid layer might be the reason.

In general, two types of viscosity are differentiated: dynamic and kinematic viscosity. The temperature-dependent dynamic viscosity is defined as the ratio of the shear stress acting on the fluid to the shear rate [227]. The kinematic viscosity is defined as the ratio of the dynamic viscosity to fluid density [231,232]. MWF-producers widely use the kinematic viscosity to characterize MWFs.

The viscosity Index VI, is a scalar value which indicates the viscosity change depending on the temperature changes. This parameter is commonly used to indicate lubricants for mechanical systems like engines or gears. Lubricants with a high viscosity index are able to maintain constant viscosity in a broad temperature range.

Due to their high molecular weight and highly branched chain architecture, polymers are suitable components to improve the viscosity of MWFs [73,210,260]. MWFs with low viscosity emit volatile organic compounds (VOC) more easily [223].

2.1.5. Complexity of the working mechanisms of MWFs

Lubrication is one of the most important tasks of MWFs in manufacturing processes. The lubricating ability is the result of a complex combination of physical aspects (e.g. capillary flow, Marangoni effect, viscosity) and chemical interactions (e.g. adsorption or chemical reaction). For example, at higher temperatures, the viscosity of a MWF decreases and thus it can be expected that the wetting ability and capillary increase. But due to the Marangoni effect the MWF flows away from the hotter zone. As a consequence of the partly opposed effect, the individual conditions of a

manufacturing process are decisive regarding the question, which working mechanism dominates. Furthermore, the specific kind of chemical interaction strongly depends on the partners within the tribological system and will be discussed in the following section.

2.2. Characteristics of metal surfaces

The type and intensity of chemical interaction of MWFs with metal surfaces is on the one hand strongly dependent on the composition, additivation and the base fluid of the MWF. On the other hand, also the chemistry of the involved metal surfaces (tool and workpiece) plays a decisive role for the effectiveness of a specific MWF.

The chemical properties of a metal surface vary considerably due to the basic composition, the presence and combination of alloying elements, the microstructure, the surrounding conditions, the type of chemical and thermal pre-treatments, etc. This section aims at summarizing the most important aspects of metal surface chemistry by means of pointing out theoretical possibilities to interact with MWF-additives. Until today, the chemical state of a metal surface in the moment the metalworking process takes place cannot be measured or predicted. Thus, the working mechanisms of MWFs and their additives have not been experimentally validated in depth so far.

The depth of surface layers relevant for interactions with MWFs and their additives are depending on the specific material and may vary significantly. The well-known effect of passivation (e.g. for aluminum or stainless steels) is based on the formation of an oxide-layer (e.g. Fe-O) [86]. Especially for steels, it is well known, that the chemical properties of the metal surface can change considerably due to the alloying elements or the boundary conditions (temperature, humidity, etc.). In the discussion of Forbes' paper [69], Hotten states: "Iron is a chameleon - it changes its skin with the surroundings". The precise description of the outer surface layer is very complex under real conditions. The metal surface is covered by hydroxyls and oxides, functional groups, in an unstable ratio depending on several parameters. Bhargava et al. have shown by X-ray photoelectron spectroscopy (XPS) that at the surface of iron samples (99.95% purity) iron oxides and iron hydroxyls were obtained [20]. In contrast, a stainless steel (X8CrNiS18-9, AISI 303) features solely oxides especially chromium oxides and iron oxides at the surface [86]. Yamashita et al. have also investigated different types of iron oxide (α -Fe₂O₃ (haematite), 2FeO·SiO₂ (fayalite), Fe₃O₄ (magnetite), Fe_{1-y}O (wüstite)) by high resolution XPS. The authors have shown that the metal surface has been oxidized only partially, which is in agreement with Kaesche, who supposed that oxides at the metal surface occur area-wide or island-shaped [104,286].

Ghose et al. described the surface structure and composition of three iron-(hydr)oxide systems under hydrated conditions at room temperature using crystal truncation rod (CTR) analysis. These investigations reveal the differences in interface structure and distribution of hydroxyl groups at surface–water interfaces which is of high relevance for water-based MWF [72]. In Fig. 16, the layer stacking sequence of α -Fe₂O₃ is presented. Furthermore, the interaction with water is indicated. The large dark gray spheres

within the material represent oxygen; the small light gray spheres represent iron atoms.

However, the chemical properties of a metal surface are not only influenced by its chemical composition but also by its microstructural properties on different scales [32,44,45,72]. The texture (polycrystalline microstructure) of alloys is considered in the size range of μm –mm and has several characterizing elements to describe the surface texture: slip planes, grain boundaries, carbon inclusions etc. [44]. Brown et al. present a simple block model focusing on the surface of a single crystal which shows a number of defects in the lattice. These defects can be the key to the chemical reactivity of metal surfaces [32]. The buckling sites, impurity atoms, steps and vacancies are leading to a higher percentage of surface phase boundaries and local distortion of lattice where active substances are able to penetrate the surface. This affects indirectly the bonding properties and thus the chemical properties of the atoms within the outer surface layers of metals.

Besides the chemical properties of the steel surfaces, especially in manufacturing processes, the material properties within the moment of processing must be considered. Freshly machined metal has the oxidation state (0) which is an "unstable" state for most metals applied in manufacturing. For this reason, the metal atoms are highly responsive for new bonds or saturation of their surface. Oxygen is one of the main partners for interactions/reactions with metals [215]. A fundamental aspect of the theory that additives in MWFs perform a chemical reaction with the freshly generated surface presumes that covalent bonds between the metal surface and parts of the additive molecules are formed. However, this type of additive working mechanism is still discussed controversially (cf. Section 2.3).

2.3. Specific MWF-components and their effects on selected processes

The chemical properties of metal surfaces differ significantly. As a consequence, the type and intensity of interaction of MWF-additives with different materials varies considerably. This is not a new finding but nevertheless, in publications focusing on MWF-performance, the metal chemistry is rarely addressed. In this section, examples of publications are summarized which are taking the interactions between the metal surface and the MWF's components into account.

De Chiffre et al. illustrated the effect of lubrication in an orthogonal cutting process of aluminum and electrolytic copper by using a tool with a specific geometry allowing for a variation of the chip contact length along the cutting edge. The specific geometry of the tool causes a side curvature of the chip into the direction of the increasing contact length in dry machining. The friction between chip and tool at increasing contact length leads to an impeded chipflow. Application of a MWF reduced the friction and led to a constant chipflow [52]. These experiments impressively indicate the strength of chemical effects in machining processes. Simply by adding a MWF, chip formation as well as the loads during machining are significantly influenced. The effects of MWF usage can furthermore be noticed beyond the process itself. Besides others, Karpuschewski and colleagues focus on the correlation between the choice of MWF in finishing operations and the running in behavior of engine components [106]. The results reconfirm that the adsorption layer and reaction layer (Fig. 8) significantly influence the functionality of metal surfaces.

The specific variation of the MWF-composition under consideration of a defined variation of the chemical properties of the metal surface was presented by Huesmann-Cordes et al. [95]. The concentration of two types of extreme-pressure additives (poly-sulphides and overbased sulfonates) was varied and the lubricating ability of the MWFs was assessed comparing their performance in tribological tests applying two types of steel. The tribotest according to Brugger DIN 51347 generates wear scars of varying size depending on the lubricating ability of the applied MWF. 100Cr6 (AISI 52100) is known to feature hydroxyls and oxides at

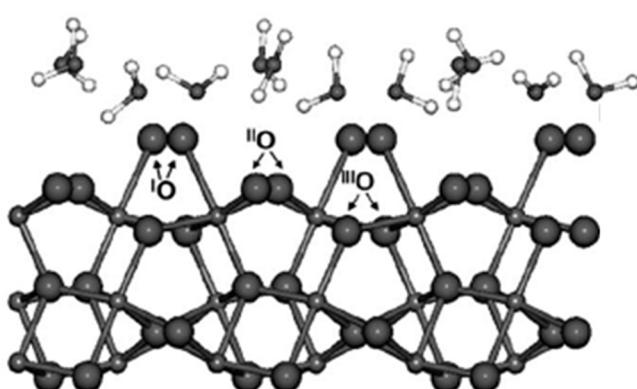


Fig. 16. Chemical surface structure of iron-(hydr)oxides as described by [72].

the surface whereas the stainless steel X8CrNiS18-9 (AISI 303) is characterized by oxides (cf. Section 2.2). The polysulphide molecules vary in their relative amount of sulphur, their activity, and the space which is required by the organic side chains. The complexity of the molecules of the polysulphides (PS) under investigation increases in following order: PS 20 < PS 32 < PS 40. With increasing complexity, less molecules of the respective PS are able to interact with the surface.

For each type of polysulphides (constant concentration of all other additives), an optimal concentration leading to a minimum of wear at AISI52100 surfaces was identified (Fig. 17). A significantly reduced lubricating ability was obtained for the same MWFs at the AISI 303 surfaces [95]. These results give a good impression about the complexity of the interrelationships between the MWF-chemistry, the chemistry of the metal surface and the lubricating ability. Small changes of one parameter may considerably influence the results in manufacturing processes. In this case, variation of the concentration of one additive easily leads to an increase of the size of wear scars by the factor of 2. Lack of knowledge regarding the correlations between metal properties and MWFs will thus inevitably lead to a loss of process efficiency and stability.

Comparable results were obtained by Niewelt, who systematically increased the additivation of an ester-based MWF and subsequently performed grinding processes. For the chosen parameters, he identified a minimum regarding the specific normal force and the specific tangential force at a certain composition of the MWF. Further addition of sulphur additives lead to an increase of the grinding forces (Fig. 18).

The results obtained in these systematic approaches are in accordance with the theory that the working mechanisms of MWF-additives are based on adsorption layers and ionic interactions which was presented by Schulz and Holweger [217]. Schulz and Holweger combined considerations regarding the specific properties of additive molecules with the chemistry of different metal surfaces and came up with an explanation for observed results from science and industry whereat chemical reactions (formation of new covalent bonds) play no role.

The theory of adsorption and ionic interactions is also discussed in context with ionic liquids (for example tetraalkylphosphonium-tetrafluoroborate), where multi-layer ionic liquid films will possibly be formed at metal surfaces [126]. These films are hypothetically layer-structured (see Fig. 19b). Here, the metal surface is positively charged so that anions are able to accumulate in a monolayer by coulombic forces. The second layer consists of cations and in this case it is assumed that additional weak hydrogen bonds may support the layer formation. Several layers form a well ordered multi-layer, which has a lower friction coefficient and leads to increased wear resistance [126,146].

In addition to the interaction between the additive molecule and the metal surface, the interactions between the additives themselves play an important role for the lubrication ability of MWFs. Already Mould et al. examined the influence of sulphur and

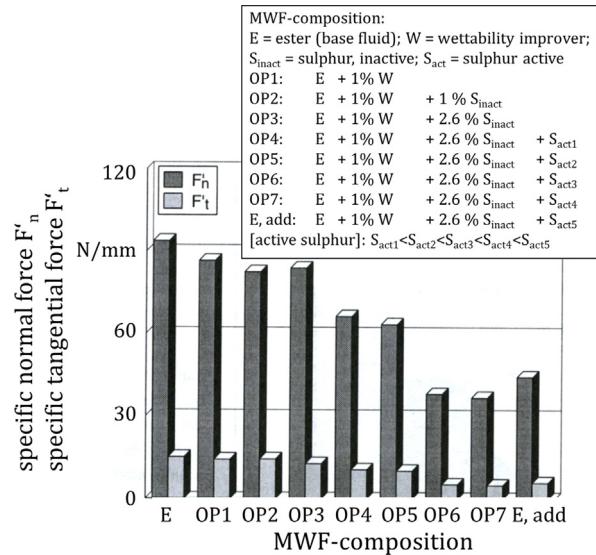


Fig. 18. Influence of the sulphur content of MWFs on the grinding forces [167].

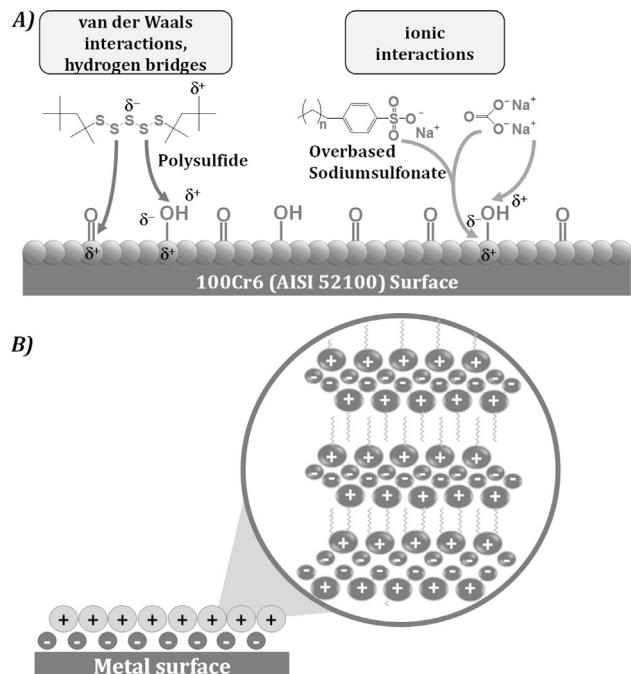


Fig. 19. (A) Possible working mechanisms of polysulphides and overbased sodium sulfonate according to the theory of Schulz [95,217]. (B) Schematic of an ionic-liquid film according to [126] and [146].

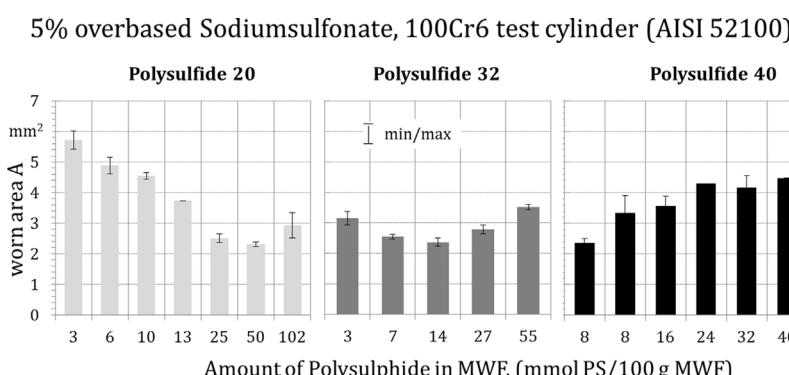


Fig. 17. Steric influence of different polysulphides (EP-additives) on the wear investigated by a wear resistance test [95].

organochlorine compounds in the same mixture. They observed a synergistic effect comparing the lubrication performance in mixtures compared to MWFs with only one additive [149–151].

Antagonistic effects have been described as well. Spikes et al. summarized the synergistic and antagonistic effects and their location with a special approach for analyzing the interactions of anti-wear-additives (ZDDP) [228]: MWFs with different concentration-ratios of phosphor-containing additives showed synergistic results [116,230] whereas mixtures with different extreme-pressure additives (sulphur-containing substances) lead to antagonistic effects [228]. Combining extreme-pressure and anti-wear additives in MWFs was found to cause more synergistic effects [47,107]. The observations were in all cases influenced by the test conditions, e.g. contact pressures [89,90] or temperature [228].

In several publications, the influence of the temperature on the lubricating ability of MWF-additives is referred to, based on the resulting friction coefficient. The graph presented in Fig. 20 was published several times [23,105,118]. It is commonly used to explain the mechanism of additives depending on the working temperature. The initial focus of the work presented by Bowden and Tabor was to identify the temperature at which reaction layers of metal sulphides and metal chlorides break-up [22,23]. However, the results of their experimental work were not presented by Bowden and Tabor in the way Fig. 20 indicates. Re-publication and improper modifications of the illustration lead to a misleading interpretation of the data [216].

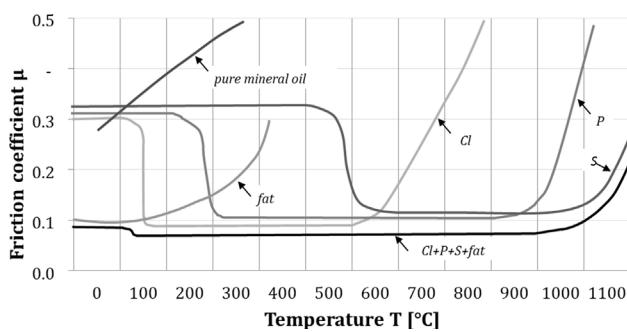


Fig. 20. Friction behavior in relation to the temperature for several additive classes according to [23,105,118,216].

Various theories regarding the working mechanism of MWF-additives exist and are under controversial discussion until today. One common assumption is the chemical reaction of sulphur compounds with the iron atoms on the metal surface to form iron sulphides. It is assumed that these iron sulphides improve the lubrication during manufacturing processes. Forbes and Reid [70] have proven the formation of iron sulphides but in this case the reaction time was exorbitantly high (up to 20 h) and not comparable to the conditions in manufacturing processes. Also Walter has experimentally verified the existence of sorption and reaction layers, which were found in the contact zone of the workpiece/chip, by ESCA investigations [259]. But it remains unclear, how long the MWF stayed on the freshly machined surface and whether the surface was cleaned after the machining. Comparable results were found in several publications in recent decades [93,94,198,219,249,290].

2.3.1. Conclusions regarding the working mechanisms of MWF-additives

In summary, the explicit working mechanisms of the different types of additives are still not scientifically verified. Recent results indicate that adsorption probably is the most important aspect of the interaction of additives with metal surfaces. The occurrence of layers resulting from chemical reactions nevertheless is a well described phenomenon. Two aspects regarding the ability of additives to build-up covalent bonds at the metal surface right in the moment of the manufacturing process should be considered: (a) the time available for an additive to perform a chemical reaction within the process might be too short. Adsorption is a much faster way of interaction. (b)

In case that additives chemically react with metal surfaces, their concentration should decrease considerably over the service life of a MWF (water-based or oil-based). In grinding processes e.g. very large new surfaces are generated especially at the small chips. This should lead to a fast drop of the additive concentration but this effect has not been observed in practice (c.f. Section 3).

3. Effects of the MWF-composition on the performance of selected processes

In Section 2, it was shown that changes of parameters such as the workpiece material considerably influence the performance of the MWF. Furthermore, the substantial influence of small changes of the MWF-chemistry on the lubrication ability was presented. Based on the awareness, that even small variation of the concentration of additives lead to noticeable effects regarding the technical performance, this section aims at reconfirming the influence of intended and uncontrolled changes of the MWFs on the process behavior.

Commercially available MWFs vary considerably regarding their chemical composition. Thus, changing the MWF in a machine tool may influence the processes performance. Section 3.1 will present some experimental data pointing out the influence of the MWF-composition on the processes' performance.

Oil-based and especially water-based MWFs are prone to changes of the MWF-chemistry over the service life. Major reasons for these aging effects are the thermo-mechanical loads during the process and microbial metabolism (for water-based MWF only). Section 3.2 summarizes the state of the art regarding MWF-monitoring and presents examples for the relationship between MWF-aging and process performance.

3.1. Intended and controlled variations of the MWF-chemistry in manufacturing processes

Regarding the effect of varying the MWF on the process performance by means of wear analyses, temperature measurements and surface integrity there have been numerous publications in the past [248,258,265,287]. These experiments and the observed differences of the performance of MWFs confirm the significance of MWFs in manufacturing processes. Evans illustrates the influence of different MWF (pure water, two types of emulsion and straight oil) on their influence on the process force in drilling P265NL (AISI1018) steel with high speed steel tools (Fig. 21).

It is obvious that the oil-based MWF leads to lower cutting forces and less increase of cutting forces over the number of drilled holes. Furthermore, this result points out that even the choice of emulsion has a clear effect on the cutting forces [68]. However, it remained unclear, which concentrations and flow rates were applied. The results presented in Fig. 22 emphasize the influence of varying MWF-compositions. In a yet unpublished study at the University of Bremen performed relating to this paper, all parameters in a profile grinding process were kept constant excluding the MWF-emulsions (5%) applied. Three different commercially available MWFs were

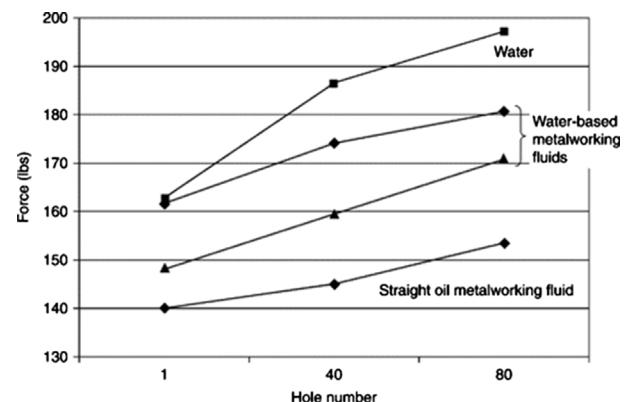


Fig. 21. Forces in drilling experiments applying different MWFs [68].

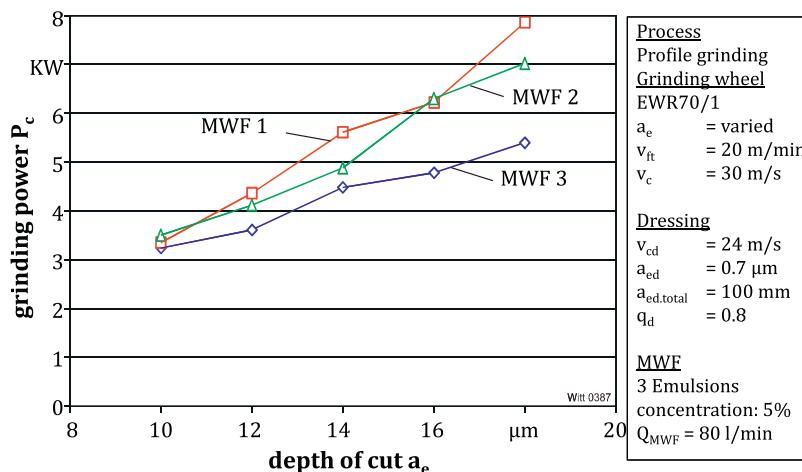


Fig. 22. Influence of the MWF on the cutting power in grinding at varied depths of cut (source: IWT Bremen).

used on the same machine tool, applying the same tool, workpiece material, grinding parameters, and MWF-supply parameters. All MWFs were specially designed three different producers for the same application (grinding of steel workpieces). However, the experiments indicate a strong dependence of the grinding power P_c from the used MWF. Especially at high depths of cut, the specific lubricating ability of the MWFs leads to significant variations of the cutting power. The example demonstrates the important role the MWF-composition, which varies slightly from product to product, with regard to the productivity of manufacturing processes.

Vits demonstrated similar effects in earlier works. He compared oil, emulsion and solutions with varied composition and stated that increasing lubricating capability results in decreasing normal and tangential grinding forces [258]. Many publications presented results, which lead to the propagation of the advantages of using oil-based MWF in grinding processes [25,111,238]. Besides of reduced wheel wear and grinding forces, improved workpiece finish is often combined with the use of oil-based MWFs [34]. However, this is not a general statement as the demands of the process vary considerably based on the chosen parameters.

Even though the use of oil-based MWFs has in some cases clear advantages, lubrication of the contact zone above a threshold can generate negative effects as an increased grain cutting depth T_μ may result. This leads to a higher portion of friction compared to chip generation accompanied by higher temperatures. Rising thermal loads of the workpiece layer are the consequence [258]. When comparing the performance of oil-based and water-based MWFs in grinding of case hardened steel 16MnCr5 (AISI5115), Heuer found that for the use oil-based MWFs tensile stress in the workpiece layer was induced (especially at high material removal rates). In contrast to this, emulsions lead in all cases to compressive residual stresses [87]. In view of thermal effects on the workpiece layer water-based MWFs have a clear advantage [287].

The presented case studies confirmed the general statement that oils have a higher lubrication ability and water superior heat conductivity. Irani et al. presented an approach to summarize and assess the characteristics of the common types of grinding fluids [99].

3.2. Influence of service life on the technical performance of MWFs

The chemistry of a MWF changes significantly over its service life. However, for oil-based and water-based MWFs, the criteria for the end of the service life differ considerably. Therefore, the effects occurring in these types of MWFs are discussed separately in the following.

3.2.1. Oil-based MWFs

Changes of the MWF-chemistry in oil-based systems mainly result from effects such as oxidation or polymerization of MWF-components. The amount and rate of oxidation is strongly

dependent on the accessibility of the MWF to atmospheric oxygen. Polymerization may occur due to thermally induced reactions. One consequence of these chemical effects is a change of the viscosity leading to impaired flow conditions in a machine tool [165,247]. Beside the chemical modification of substances within the MWF, volatile substances evaporate especially at higher temperatures (impact load in the contact zone or high temperatures within the MWF tank at high productivity) and thus cause a decrease of the concentration of the MWF-component [144].

Additional changes of the chemical properties of MWFs in oil-based systems result from the contact of the MWF with the tool and workpiece material [13]. In grinding processes, small particles of the grinding wheel as well as the chips provide a considerable surface area. The transfer of metallic-ions into the MWF or MWF-components to the surface carries the potential for a noticeable shift within the MWF-chemistry. Significant changes of the chemical composition are also obtained when leakages lead to the contamination of MWFs e.g. by hydraulic fluids.

3.2.2. Water based MWFs

Besides the effects for oil-based MWFs, which also apply to the water-based MWFs, the presence of water leads to a number of additional chemical and microbial alterations. As the oil-based systems appear to be more stable, water-based MWFs are monitored on a regular basis. European employers' liability insurance associations recommend a weekly monitoring interval for MWFs in a running system and starts with a control of the water, which is used to prepare the new MWF. Parameters which should be tested before the MWF is prepared are e.g. the pH-value, conductivity, water hardness, nitrite-/nitrate-/chloride-concentration and microbial contamination of the used water [203]. In case that these tests reveal unfavorable properties, an early loss of the MWF's performance must be expected.

As premature aging of water-based MWFs is accompanied by effects such as corrosion (Fig. 23) of machine tool components and workpieces, microbial and health issues, as well as higher costs for disposal and refilling, a systematic monitoring is of high importance. The following sections aim at presenting the most relevant monitoring methods and parameters as well as at

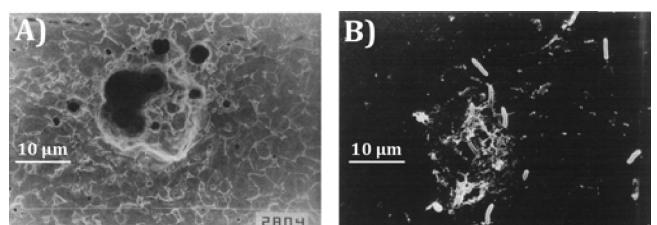


Fig. 23. (A) Microbial induced corrosion (MIC) induced by (B) bacteria forming extracellular polymeric substances (EPS) and biofilms at the surface [171].

discussing the changes of these parameters against the background of the MWF performance.

3.2.3. MWF concentration

Depending on the manufacturing process, water-based MWFs usually have a concentration within the range of 3–10% (MWF-concentrate in water). The concentration of MWFs can change over the service life significantly due to antagonistic effects. An increase of the concentration can result from the evaporation of water. Especially working at elevated temperatures e.g. in summer and/or at high productivity, can lead to an increase of the MWF-concentration by several percent a week. A decrease of the MWF-concentration is observed when large amounts of the oil adhere to chips or workpieces. This leads to a continuous discharge of the oily fraction of the MWF. As many additives are lipophilic and thus solved in the oily parts of the MWF, the concentration of the additives decreases as well. This has a substantial effect on the technical performance of the MWF as the deviations of the concentration of certain additives are larger than the controlled variations presented e.g. in Section 2.3.

The MWF-concentration commonly is assessed using a refractometer. This hand-held device allows for easy measurement of the refractive index of the MWF, which can be correlated with the MWF-concentration.

3.2.4. pH-value

In general, the pH-value of water-based MWFs (emulsions or solutions) should be in a moderate alkaline range ($\text{pH} = 8.0\text{--}9.5$) to avoid corrosion of machine tool elements and to reduce microbial load. These MWFs are buffered systems to allow for higher stability of the pH-value. The pH-value represents the negative decimal logarithm of the hydrogen ion (H^+) activity and is mainly influenced by microbial processes. In many metabolic pathways of microorganisms, H^+ -ions are released into the surrounding media which leads to a decrease of the pH-value.

Values lower than 8.0 are accompanied with the risk of machine/workpieces corrosion, emulsion instability and the formation of carcinogenic *N*-nitrosamines (see below). High pH-values above 9.5 are also reported to lead to skin irritation [36,246]. Consequently, the pH-value should be assessed on a regular (at least once a week) base. Common measurement techniques are pH-meters based on electrodes or pH-paper. The latter show a comparably poor resolution.

3.2.5. Nitrate/nitrite concentration

Lower levels of nitrate and nitrite concentration in water-based MWFs may result from contaminations of the used water and/or additives such as nitrated biocides. Higher concentrations in most cases result from microbial activity and are thus a strong indicator for the proliferation of microorganisms. However, the practical relevance of this parameter is independent from the microbial load but related to health issues. The presence of primary and secondary amines (or alkanolamines, e.g. ethanolamine, diethanolamine (DEA)), which act as pH-stabilizers, surfactants, or corrosion inhibitors in MWFs, is accompanied by the risk of the formation of *N*-nitrosamines [236,272]. *N*-nitrosamines may be formed at conditions such as extreme heat and pressure generated by manufacturing processes: nitrate can be reduced to nitrite, which reacts with amines to the corresponding *N*-nitrosamine. Also secondary amines are able to react with nitrogen oxides (NO_x) from the air or nitrites [10,156]. In Fig. 24, the reaction mechanism of the *N*-nitrosamine formation is shown.

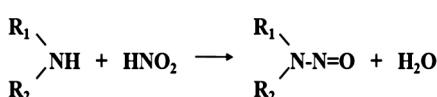


Fig. 24. Formation of *N*-nitrosamine by reaction between secondary amines and nitrites [164].

The critical value is 50 mg/l for nitrate concentration and 20 mg/l for nitrite concentration [252]. Common measurement techniques are based on simple test strips and an optical evaluation.

3.2.6. Emulsion stability

The commonly mean droplet size of MWF-emulsions is 0.1–2.0 μm depending on the machining parameters and composition of the MWF. Aging of an emulsion leads to a change in the composition and thus the droplet size changes. Furthermore, the size distribution becomes wider (see Fig. 25). Uncontrolled aging of MWF-emulsions is reported to lead to complete phase separation due to biological (metabolism), chemical (salt/acid contaminations), and thermal (machining) impacts [74].

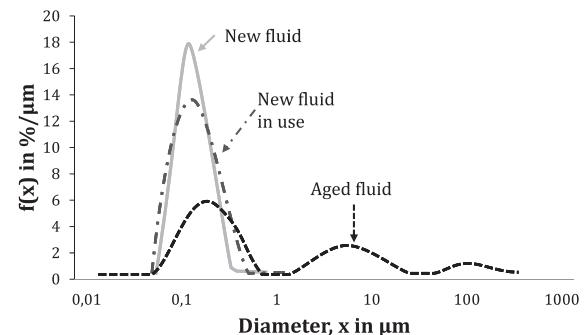


Fig. 25. Proportional frequency of the droplet size ($f(x)$ in %/ μm) indicating the droplet size distribution and the aging behavior of a MWF emulsion [74].

Zimmermann et al. investigated the influence of ion accumulation on emulsion stability and MWF service life. It was shown that higher salt concentration, resulting e.g. from hard water salts, lead to an increase of the mean droplet diameter from 0.02 μm to 2 μm . Furthermore, it was found that the microbial colonization was accelerated. Stable nanoscale emulsions may improve microbial resistance and MWF longevity [185,291]. However, the lubricating ability in a tapping-torque test improved with increasing droplet diameter whereas the performance in machining experiments was not influenced. At mean particle diameters higher than 3 μm phase separation occurred.

Several methods can be used to investigate and assess the stability of water-based MWFs: the dynamic light scattering (DLS) allows the characterization of droplet size distribution and coagulation rate. The Zeta potential quantifies the emulsion stability by measurement of the particle charge. Analyses of the turbidity reveal the droplet size distribution e.g. by optical measurements [42,74,196].

3.2.7. Microbial aspects

The main parameter leading to premature aging of a water-based MWF is its colonization by microorganisms (MO). The microbial contamination of MWFs is in the focus of scientific publications since the last century [15,124,176,185,206,255]. Two effects caused by microbial growth have to be considered regarding the performance of MWFs: the formation of biofilms and the metabolism of MWF-components.

Biofilms [171,251] are the preferred way of living for most microorganisms such as bacteria, yeast or fungi. They consist of the living cells and surrounding polymeric substances called extracellular matrix. This matrix is actively produced by the MO and leads to several advantages for the cells: protection against biocides, exchange of nutrients with other cells, the formation of a synergistic community of different species, and many more. Noticeable effects of biofilms in MWFs are e.g. macroscopic biofilms in MWF-tanks (Fig. 26A), clogging of pipes and filters (Fig. 26B), microbial induced corrosion of machine tool components and a certain odor of the MWF [173]. As this paper focuses on the influence of chemical changes within a MWF, these macroscopic effects are not discussed in further detail.

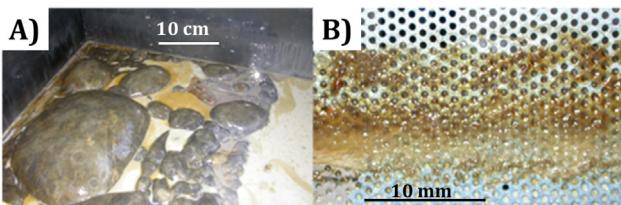


Fig. 26. (A) Macroscopic biofilms in a MWF-tank and (B) filter clogged by biofilms [143].

The usage of MWF-components as carbon- and energy-sources by microorganisms may cause significant changes of the MWF-composition. The large variety of MO leads to a situation which makes it nearly impossible to identify suitable additives, which cannot be metabolized by bacteria or fungi. As a consequence of the metabolism, the concentration of desired MWF-components decreases over the service life whereas products of the metabolic processes accumulate. Fig. 27 exemplarily summarizes some effects during the service life of a water-based MWF. With increasing microbial load (colony forming units CFU), the concentration of a selected additive (monoethanolamine, MEA) drops. Furthermore, the technical performance (here, the avoidance of tool wear) diminishes. Further studies revealed an increasing risk of microbial induced skin damage and infections [233].

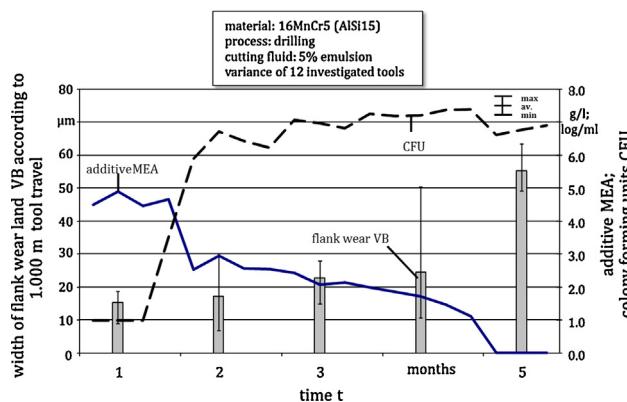


Fig. 27. Influence of the microbial load on the technical quality of MWFs and tool wear in drilling [143].

An inversion of the paradigm that microbial activity in MWFs cause negative effects is investigated by Brinksmeier and colleagues. In an interdisciplinary approach, the potential of bacteria and/or microbial products to act as MWFs or at least substitute MWF-components was revealed. The lubrication ability of bacterial cells was shown to be superior to commercially available MWFs under certain circumstances [194,195]. This approach goes beyond the concept of a European MWF-producer to add one bacteria species to emulsions on purpose to avoid settlement of further, undesired species.

To reduce negative effects of the microbial contamination, various methods are available. The wide use of biocides such as formaldehyde releasing agents is suitable to delay the microbial colonization. A complete avoidance even in well cleaned systems is almost impossible due to the exceptional properties of MO. Other methods to control the microbial colonization such as ultraviolet light [208] and gamma radiation have been shown to feature high expenditures and/or low antimicrobial efficiency [63,175,205].

Various methods exist to estimate the quantity of MO in MWFs: dip slides, adenosine triphosphate (ATP) measurement by enzymatic luminescence spectroscopy, measurement of dissolved oxygen, and catalase tests [39]. In the past, dip slides were used as a simple method to determine the microbial contamination. However, the test takes at least 24 h or longer to incubate before the amount of CFU can be assessed. Additional limitations of the

methods derive from the used type of nutrient media and the way of taking the sample: anaerobic MO, slowly growing MO or MO from biofilms within the pipe-system of a machine tool will not be detected [176]. The determination of bacterial load based on the concentration of the universal energy carrier ATP correlates with the biological activity of MOs in the MWF [177]. However, the direct measurement of the number of CFU is not possible as inactive (but living) cells do no produce significant amounts of ATP. Nevertheless, the ATP test is discussed to be suitable for real-time control and it detects all metabolically active MO in the sample [39].

3.2.8. Demand for automated control systems

To allow for high productivity and to work at high resource efficiency, long service life of water-based and oil-based MWFs must be achieved. Especially the knowledge on the microbial and chemical properties of a MWF is of high importance for the end-user. Until today, the monitoring methods described above are the only established tools for a regular monitoring of the MWF-condition. These techniques are often time consuming, prone to deviations due to inter-observer effects, and suffer from poor accuracy. An approach to automate a demand-oriented MWF-control was presented by Palmowski et al. [173]. The authors aim on developing a closed loop control allowing for the systematical combination of (conventional and advanced) sensors with maintenance methods. This would allow for e.g. the adjustment of the additive concentration or the addition of biocides without the user taking any action. Fig. 28 illustrates the idea of closed loop online control and demand-oriented maintenance of MWFs presented by Brinksmeier and colleagues.

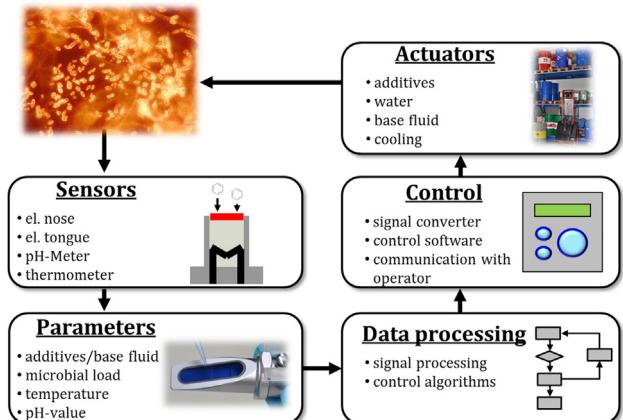


Fig. 28. Approach for online closed loop control of MWFs using advanced sensors such as an electronic nose [144].

One possibility to allow for online measurement of the chemical and the microbial state of MWFs are electronic noses or tongues [112,202]. However, these sensors have to be calibrated. Preliminary work on this issue has been presented in the last decade [185,270]. Recent findings based on GC-MS (gas chromatography with mass spectrometric detection) revealed that suitable marker-substances can be identified. The application of corresponding sensors might allow for the online-detection of changes within the MWF-composition and thereby improve and facilitate MWF-monitoring and maintenance [173].

4. Advanced approaches for sustainable MWF-application

Recent and future challenges in the application of MWFs are economically and environmentally driven. To achieve higher productivity and resource efficiency, two aspects of MWF-application are decisive: the possibility to apply MWFs as multipurpose fluids and the increased sustainability of MWFs. This section aims on giving an overview regarding today's trends and possible future developments.

4.1. Multipurpose MWFs and MWFs with multiple functions

Metalworking fluids applied today fulfil multiple objectives. In this context, the terms “multipurpose MWFs” and “MWFs with multiple functions” is used. The term multipurpose MWFs describes the use of the fluid for different applications, while in each application, one MWF can also have multiple functions. This interrelationship is presented in Table 4. The level of application (left column in Table 4) can be subdivided into:

- **Unit process:** e.g. material removal or forming process
- **Machine tool:** device which performs the unit process
- **Process chain:** logical organization of machine tools and supporting equipment e.g. filtration or cleaning systems.

On each level, the fluid can have one or more functions. On the first level, the MWF is applied to support and facilitate the unit process. The related functions are cooling, lubricating, cleaning, processing and insulating/conducting. In addition, on the machine tool level the MWF can serve to facilitate the component movement and holding as well as the process monitoring and control adding the functions of power and signal transmission. On the process chain level, the MWF can be used in various unit processes and machine tools (e.g. turning, milling, grinding, honing, etc.) as well as different materials (metallic and non-metallic). For example, Joksch reports about the MWF use in a process chain with different machining operations to produce automobile crank shafts [103]. The multi-functional utilisation is achieved by using the oil-wetted parts and chips from a deep hole drilling process to produce a high performance emulsion. For this purpose, the wetted parts and chips are washed inside a cutting fluid filter filled with water to create the emulsion [103]. This approach leads to nearly oil free parts and chips and to an increased resource efficiency of the fluid use. In the following, for each function an example is described in more detail.

4.1.1. Processing function in machining

In machining with geometrically defined cutting edge, the MWF can be applied to the contact zone with a pressure level between 2 and 400 MPa [209]. The high fluid pressure supports chip breaking and reduces tool wear [181]. The fluid is either applied directly into the chip-tool interface through/alongside the tool rake face [131,181,187], between the clearance of the tool and the workpiece [60], a combination of both [218], or is used to break the

chips outside of the contact zone [190]. The fluid supply, through/alongside the tool rake face, is the most common one. The high pressure supports a deeper penetration of the MWF into the contact zone, and consequently increases the cooling and lubricating efficiency. Commonly, mineral-oil-based emulsions are applied [209]. Investigations of Nandy et al. showed that the application of a mineral-oil-based emulsion compared to a neat mineral-oil leads to a significantly reduction of wear by at least 143% and compared to conventional flood lubrication to a lower wear rate of at least 250% [161].

Besides chip breaking, the high pressure application of MWFs can also be used for deburring, edge rounding, surface smoothing and surface hardening [113]. In the case of deburring, water-based or oil-based fluids can be applied with a pressure between 30 and 80 MPa [88,263]. A further high pressure application is the use of the MWF for tool cleaning to prevent, for example, grinding wheel clogging. The fluid is applied with up to 6 MPa pressure onto the grinding wheel surface [122]. By this measure, the tool life time increases, the forces are reduced and the workpiece surface roughness improves [38,85]. Investigations of Heinzel and Antsupov showed that the cleaning efficiency is influenced by the nozzle design, the orifice area and the jet opening angle [85].

However, for all of these applications the used MWF has to be composed in a way that allows for high pressure application. Possible problems such as foaming and decomposition of the fluid must be avoided [3,209].

4.1.2. Processing function in forming

In hydroforming processes of shells, sheets, and tubes, the MWF can be used as the forming/pressure media [119,212]. The fluid can be applied as a punch, a draw die, or an assisting option to improve the workpiece formability [119]. Due to its application, the frictional force and the tool costs are reduced. Furthermore the quality of the workpiece surface and the limit drawing ratio can be increased [119,166,212]. The composition of suitable MWFs must have a high similarity to hydraulic fluids with a low flammability (HFA) on water basis. Therefore, especially water-based emulsions with an oil-content of max. 20% are commonly used [166,249]. However, also oil-based MWFs are applied [81,160]. The applied fluid pressure in sheet hydroforming is about 30 to 150 MPa and about 400 to 600 MPa in tube hydroforming [119]. The fluid selection depends on the workpiece and the approval of the press manufacturer [166].

Table 4
Exemplary application area of multifunctional metalworking fluids in machining.

Level	Purpose	Function	Example
Unit process	Support and facilitate the metal removal process and the forming process	Cooling Lubricating Cleaning Processing Insulator/conductor	(1) (1) (1) (2) (3)
Machine tool	Facilitate component movement and holding	Lubricating Cooling Power transmission Signal transmission	(4) (4) (4) (5)
Process chain	Process monitoring and control	MWF functions in a unit process or machine tool	One MWF for different unit processes and materials Creating an emulsion during the cleaning of oil wetted parts and chips.

4.1.3. Insulating/conducting function

In electrical discharge machining (EDM) the fluid functions as a dielectric fluid in order to enable the spark discharge between anode and cathode, while in electro chemical machining (ECM) the fluid functions as an electrolyte. Both processes can be used for die and mold making, prototyping, etc. [117,189], but also for machining processes such as grinding or dressing of metal bonded grinding wheels [267]. In the last-mentioned EDM processes, the MWF has to be composed in a way as to fulfill the demands of cooling, lubricating, and cleaning as well as fulfilling the dielectric function. Useable fluids are full synthetic water-based MWFs [213], pure water, kerosene, and similar kinds of oils [140] as well as emulsion mist [121]. However, the fluid must have a low electrical conductivity in order to create a dielectric field between the tool and the workpiece [213]. There are even machine tool concepts in the market, where grinding and rotational EDM is done in the same set-up with the MWF acting as coolant in grinding and dielectric in EDM machining. In ECM processes, the fluid is characterized by a high electrical conductivity to enable the electrical current flow between tool and workpiece. Full synthetic water-based MWFs can be used [114], but also solutions of NaOH, NaCl or NaNO₃ [139]. A combination of both processes is electro chemical discharge machining (ECDM). For this process the MWF needs to satisfy the different demands regarding the required conductivities of EDM and ECM [213].

4.1.4. Lubricating, cooling and power transmission function

A huge variety of fluids are applied for different purposes in a machine tool. Beside the MWF for the unit process, fluids are used for power transmission (hydraulic fluids, tailstock fluid, etc.) and for lubrication of components (slideway, spindle, bearings, recirculating ball screw, transmission, compressed air, etc.). The fluids differ in dependency of their application scope in their composition and viscosity. A challenge in the application of multipurpose MWFs is to meet the different requirements. Starting point for the application are the considerations of fluids with similar viscosities and requirements. With MWF-in the centre of interest a high similarity with hydraulic fluids as presented in the case of the forming fluid exists. The use of the same fluid for both purposes can help to prevent fluid contamination, e.g. when the MWF is mixed with the hydraulic fluid due to leakages in the hydraulic system. In general, contamination results in a reduced service life and a changed composition of the MWF (Section 3.2). Reports indicate that either the application of water-based fluids [163,281] or oil-based fluids [91,174] as hydraulic fluids are possible. For example Pandey et al. report the application of a multipurpose MWF for hydraulic power transmission and for gear cutting processes. The application is supported by the high similarity of the hydraulic and MWF with regard to lubricity and wear protection [174]. Beside the hydraulic fluid, Suda et al. presented a combined approach to use the same fluid for spindle, slideway and hydraulic components as well as the cutting process [235]. For this purpose a glycol ester with a kinematic viscosity of nearly 32 mm²/s was used as base fluid and enhanced with additives [235].

In fluid-driven spindles, the MWF serves to power a spindle for rotational movement in cutting and deburring processes, for linear movement in broaching processes, or for a self-compensating tool holder [214,276,288]. The fluid-driven spindle is an additional unit that can be attached to a main spindle with internal fluid-supply. The fluid-flow through the main spindle powers a turbine inside the additional fluid-driven spindle [276,288]. The rotational spindle speed depends on the fluid pressure and it can reach rotational speeds of up to 30,000 rpm, when applying 3.5 MPa fluid pressure [214]. An advantage of this multipurpose use is the extension of the machine tool capabilities.

4.1.5. Signal transmission function

The MWF can be used for process monitoring and controlling by closing a detection circuit, by metering changes in the fluid flow rate, pressure and velocity or by the fluid transported acoustic emission

(AE) signal. For example, in deep hole drilling the fluid flow rate and velocity through the tool can be used to detect tool breakage [168] or to adjust the tool feed to prevent tool failure [21]. Another approach to detect tool breakage in drilling is the set-up of a break detection circuit. For this purpose, MWFs can be supplied directly at one side of the tool, while on the opposite side, a vibration or pressure sensor is placed. As long as the tool is intact, the circuit is interrupted. If it is closed, a tool failure was detected [1368]. A further use of vibration sensors to monitor the process is the measurement of AE signals which are transported via the fluid [97,98,168,266]. For example in grinding the fluid coupled AE signal can be used to detect process malfunction [97], to assess in-process surface roughness, [77], to analyse wheel load [61], wheel chatter [41], wheel wear [237], or contact detection, and grinding burn [266].

4.1.6. Conclusion multipurpose fluids with multiple functions

The aforementioned examples show that the use of multipurpose MWFs and MWFs with multiple functions is already established in some cases due to its potential for increasing the:

- *Productivity on unit process and machine tool level*, by improving the tool life time, enhancing the machine tool capability and reducing fluid-related machine breakdown times.
- *Stability and reliability on all level*, by reducing contamination problems (e.g. the MWF is contaminated with hydraulic fluid) and by easing process monitoring.
- *Overall efficiency on machine tool process chain level*, by consolidating different fluids in a machine tool to one fluid, by integrating different unit processes of a process chain in one machine tool or by a harmonized use of MWFs along the process chain.

It can be expected that new compositions will allow for combining even more functions in one fluid in future. Furthermore, MWFs which exploit the full potential based on the chemical contexts in Section 2 will be able to open up new fields of application in metalworking.

4.2. MWFs based on green chemistry

As mentioned in Section 1.1, the history of MWFs goes back to the beginning of civilization. Since then, MWFs were mainly based on animal fats as well as vegetable oils from various sources [62]. Climate conditions and differences in vegetation lead to a broad spectrum of regionally specific base fluids for MWFs. Later on, the composition of MWFs was strongly influenced by the discovery of petroleum. Since then, mineral oil-based components replaced the formerly popular animal and vegetable oil-based MWFs leading to more or less one single base fluid for the majority of MWFs [62]. However, a renaissance of renewable and supposedly more environmental conscious MWFs started in the early 1980s. Regionally grown or available oils and fats have been investigated regarding their suitability as MWF base fluid. This development was driven by a rise in awareness for MWF-induced occupational health problems and the limitation of fossil resources [92].

4.2.1. Environmentally adapted lubricants

Bay et al. discuss environmentally benign tribo-systems for metal forming [12]. Analogously, environmental problems in metalworking can be subdivided into the following areas: (a) health and safety of people, (b) influence on the metalworking process, machinery and periphery, and (c) recycling and/or disposal of waste and remaining products. In parallel, improvement efforts for MWFs are also focused on (1) elimination of hazardous chemicals and simplification of MWF compositions, and (2) increased resource efficiency, including longer tool life/MWF service life, recovery and reuse of MWFs and minimal quantity lubrication (MQL) [12]. These approaches are well in line with requirements defined for environmentally adapted lubricants (EAL) e.g. by [169] and [179]. They identified the following aspects

as constituting criteria for EALs: (1) Biodegradability, (2) toxicity, (3) relative content of renewable raw material, (4) functional performance during use phase and (5) favorable environmental performance over the whole life cycle (from raw material production through MWF blending and use to recycling or disposal). These developments are mirrored for example in the exhaustive list of EU Ecolabel criteria requirements for lubricants [66,159].

4.2.2. Renewable base fluids

An impressive number of raw material sources have been utilized as MWF base fluid so far. Fig. 29 shows possible base fluid sources for oil-based MWF and Fig. 30 for water-based sources respectively. In both cases, natural and synthesized oils can be distinguished while those two groups both include products based on mineral oil as well as on renewable materials. Synthesized esters received from a vegetable or animal triglyceride (e.g. rapeseed oil, palm oil, animal fat) and an alcohol are the most common renewable base fluids so far. They "... 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 technological performance level needed and composition to satisfy the environmental aspects demanded of EALs" [179]. In Fig. 29 the relevance of esters becomes obvious for oil-based MWFs by their large number and share of identified options. Examples are presented e.g. by Dettmer, Oliveira and Alves, Lawal et al. [56,123,170].

For water-based MWFs presented in Fig. 30, synthesized esters are also important, but there is a higher diversity of principally suitable fluids. For example, Winter and colleagues have worked on MWF-solutions based on glycerol [277,278] and on biopolymers [280]. Lately, another polymer (gelatine)-based MWF-solution was investigated [262]. In addition to renewable fluids, ionic liquids and re-refined MWFs get attention as base-fluids for

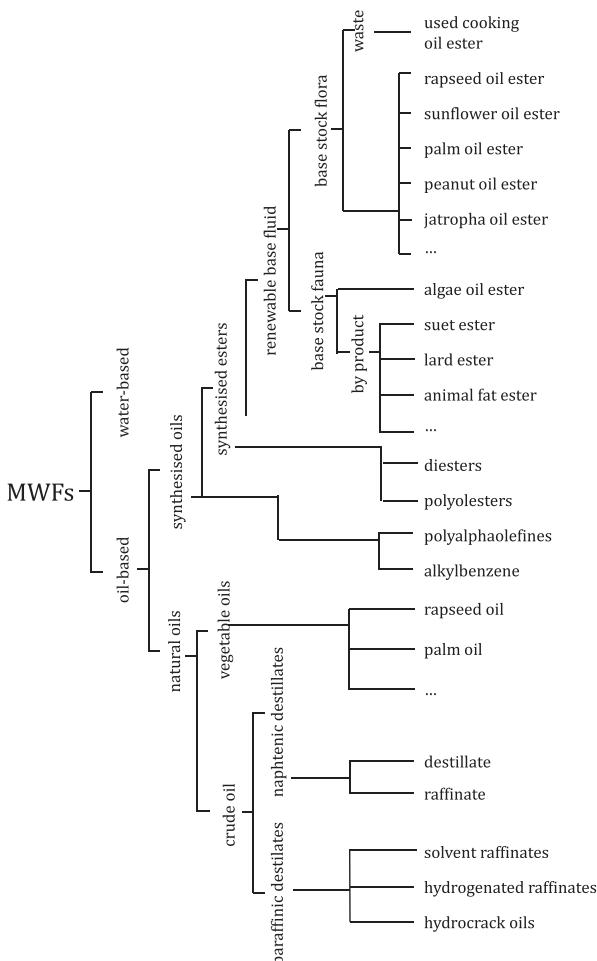


Fig. 29. Types of oil-based MWFs.

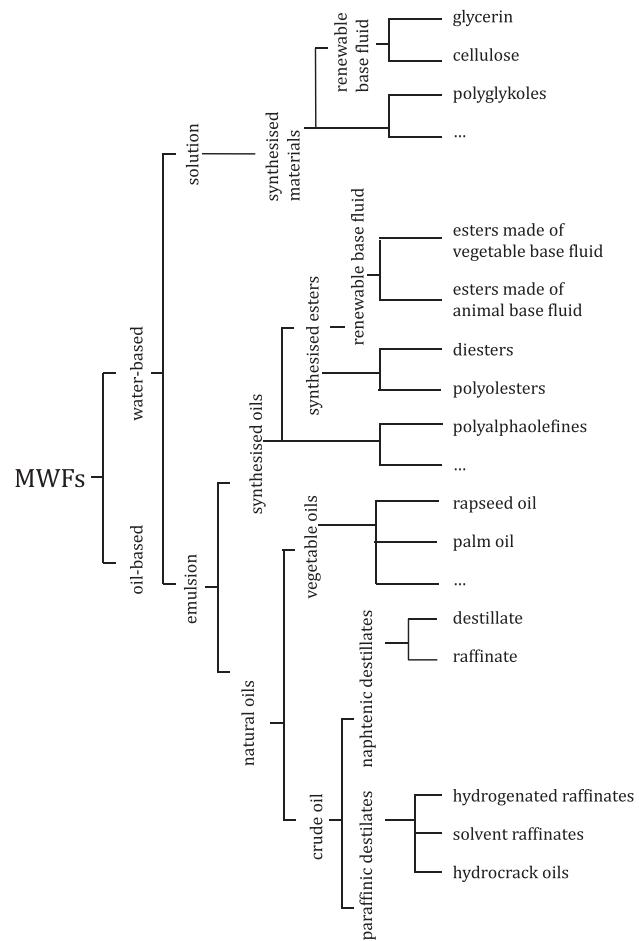


Fig. 30. Types of water-based MWFs.

MWF-solutions (e.g. [179,180,234]). Furthermore, nano particles, sulphurised fatty acids and again ionic liquids are introduced as alternative additives [55,234].

4.2.3. Evaluation of environmentally adapted MWFs

According to the set of constituting criteria for EALs, environmentally adapted MWFs have to be evaluated not only regarding their technological and economic performance but also regarding the environmental impact caused along their life cycle. Besides the traditional characteristics, the technological performance includes the necessary amount of MWF to fulfill the desired function over a certain period of time as well as any effect on other components of the tribological system (tool life, filter system, energy demand etc.).

The resulting material and energy flows directly influence the Total Cost of Ownership (TCO) for the MWF-user and environmental impacts linked with the MWF. Life Cycle Assessment [153] and Life Cycle Costing from user (TCO) or producer perspective represent established methods for such a life cycle spanning evaluation of environmental impacts and costs related to a product or service/based on the material flows induced by the product system under investigation.

Different authors have documented an equal or even superior technological performance of EALs based on renewable materials compared to conventional mineral oil-based MWFs, including higher workpiece quality, reduced tool wear, longer service life and lower quantities of required MWF [14,56,278,279]. However, these are case specific results and depend on the whole tribological system. Tribological tests (e.g. Reichert wear test) are suitable to prove general lubricating ability of environmentally adapted MWFs, whereas subsequent testing in machining processes investigates their effects on process quality and tool wear in more realistic boundary conditions. Fig. 31 displays wear areas from Reichert wear test of a grinding oil, a polymer dilution and a mineral oil emulsion,

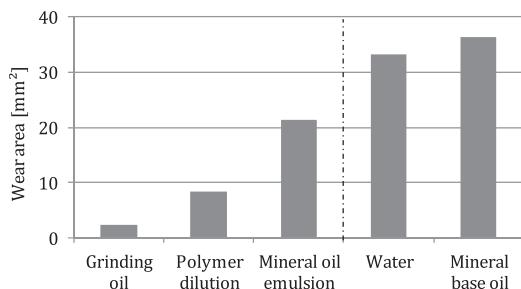


Fig. 31. Results of a Reichert-wear test from different types of MWFs [279].

supplemented by results for water and the mineral base oil (without additives). The polymer dilution can compete with the grinding oil and clearly outclasses the mineral oil-based emulsion. Water and mineral base oil in a pure condition (without additives) show poor performance resulting in the largest worn areas.

The technological potential mentioned above result in chances to compensate the comparatively high market prices of environmentally adapted MWFs. Life Cycle Costing (LCC) is designed to take follow-up costs into account and to provide transparency about costs over the whole product life cycle. Thereby, it can help to justify spend-to-safe decisions in a purchase price driven environment.

A TCO comparison of conventional and environmentally adapted MWFs that deliver the same functionality reveals whether there is an economic break-even to be expected over the MWF's service life time or not. In such a comparison, not only obvious differences e.g. in the required amount of MWF-quantities but also secondary effects should be considered as the MWF can for instance influence machine tool energy demand, tool life.

A case study presented by Winter et al. investigated the influence of different MWFs on the process energy demand and costs [283]. The study showed that the application of different mineral oil based and free cutting fluids results in varying process energy demands and costs. The case study further highlighted that the energy costs (73%) make up for a much higher share of the process costs than the MWF costs (27%). On this basis Fig. 32 shows a sensitivity analysis to assess the influence of the procurement price for three EALs and a mineral oil based emulsion in comparison to the price for grinding oil. The results show that the application of each mineral oil free cutting fluid could improve the economic performance. Cost savings between 1% (jatropha oil) and 7% (mineral oil based emulsion) could be achieved in comparison to the conventional grinding oil. Therefore, a mineral oil free cutting fluids could be more expensive and still this would result in lower or same costs (intersection x-axis = break-even point) [283].

A number of Life Cycle Assessments (LCAs) have been published on lubricants based on mineral oil or vegetable oils and other renewable materials (e.g. [141,178,254,274,275]). Recently published studies, for instance, include Roiz's and Paquot's work on chainsaw oil [204] and Raimondi et al.'s on engine oils [188].

However, only few references address MWFs in specific. Dettmer [56] as well as Winter and colleagues [273,280] compared different types of MWFs. Miller et al. analysed life cycle impacts of

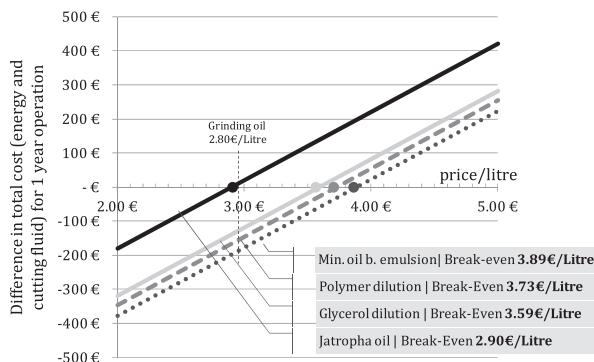


Fig. 32. Economic comparison of different types of MWFs [283].

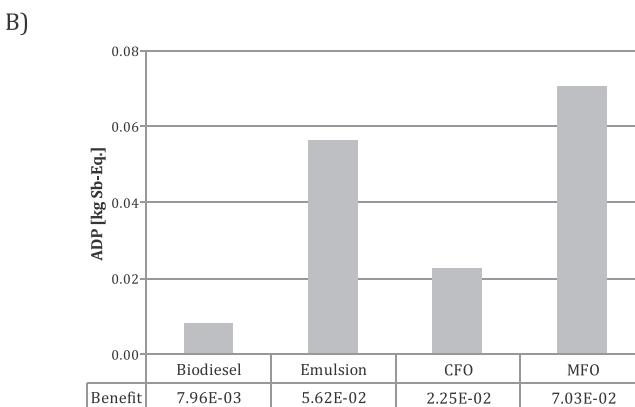
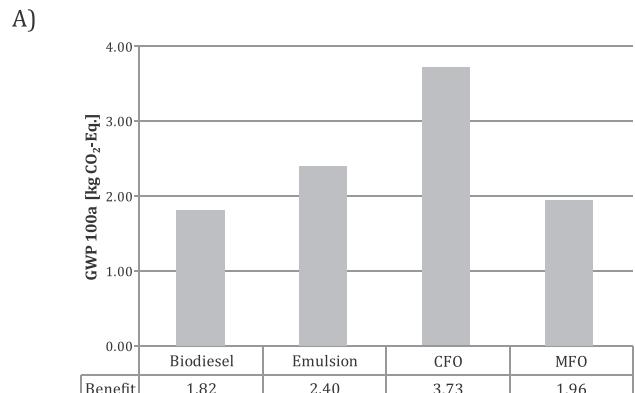


Fig. 33. Environmental benefits of different jatropha oil applications (CFO cold form oil, MFO multi-functional oil) per kg jatropha oil when compared to their associated conventional products for (A) Global Warming Potential (GWP100a) and (B) Abiotic Resource Depletion Potential (ADP) [57].

MWFs for aluminium rolling [145]. Other authors observe only parameters related to MWFs' use phase (e.g. volatility—[180]) or end-of-life options [128,148].

Most of the Life Cycle Assessments reveal a clear advantage of MWFs based on renewable resources compared to their conventional, mineral oil-based equivalents. As an example, Winter et al. compared the environmental impacts of a jatropha oil emulsion and a conventional mineral oil emulsion. They revealed a clear advantage for the emulsion based on the renewable resource jatropha oil [282].

In this case, the main effect was observed in the impact category abiotic resource depletion (ADP).

In addition, Dettmer et al. showed that twice the amount of greenhouse gas (GHG) emissions can be saved when jatropha oil is applied in MWFs like cold form oils instead of using it as biodiesel base fluid (Fig. 33) [57]. The environmental benefits are even higher when it comes to abiotic resource depletion (ADP).

Technological advantages of highly performing EALs based on renewable materials bear the chance of overall savings of costs and environmental impacts. For a comprehensive evaluation not only the whole MWF life cycle but also the whole tribological system (including tool, peripheral components like filter systems and their respective energy demands) need to be considered. Accordingly, results and identified optimization potentials are highly case specific with the lubricant base stock and use phase material flows being the most influential parameters.

5. Summary and future directions

Metalworking fluids are one of the most complex factors in manufacturing processes. The findings in literature clearly indicate their significant influence on the process productivity as well as a substantial impact on energy- and resource efficiency. The full potential of MWFs can only be exploited by understanding the multi-disciplinary interrelationships addressed in this paper. Considering

the technological relevance of small changes within the MWF-chemistry, the results of manufacturing processes can only be understood, optimized and predicted based on knowledge regarding

- the MWF's chemistry,
- the microbial state of MWFs,
- the chemical properties of the concerned metal surfaces,
- the physical conditions during manufacturing processes, and
- the possibilities of chemical substances to interact with metal surfaces.

The complexity of the topic is one of the main reasons why until today the working mechanisms of MWF-additives are not fully understood. The work cited here gives an overview of the current theories and presents data which indicates the validity of an approach which focuses on adsorption rather than chemical reactions. Aging effects in water-based and oil-based MWFs are hard to control from a chemical point of view. The changes of the MWF-composition accompanied by e.g. microbial activity have several effects on the performance of MWFs. Thus, high attention should be paid on monitoring and maintenance of MWFs. Until today, the available methods for the control of MWFs are based on imprecise measurements and long measuring cycles. The changes caused by microorganisms at high activity within one week may have severe consequences on the performance of the MWF. Future work should therefore focus on online measurement techniques with high accuracy allowing for reliable conclusions regarding the MWF's condition.

Furthermore, the application of alternative MWFs which cover multiple purposes or functions will be an emerging trend. Based on the understanding, which components are definitely required in a MWF to fulfill a certain function, the production of simplified MWFs should be possible. Knowledge-based combination of suitable substances should moreover allow for using single MWFs for several applications. Tools such as the life cycle assessment will reveal further potential regarding the substitution of fossil substances by renewable alternatives. MWFs are thus a noticeable factor for the improvement of the energy and resource efficiency in manufacturing processes.

Despite the big influence of MWFs on the results of manufacturing processes, their role is strongly underestimated in a large number of published scientific works. In many papers, no or only little information on the MWF (e.g. "oil", "emulsion", "dry") or its supply (e.g. "MQL", "flooding") is given. Taking into account that the references cited in this paper prove the noticeable effects of variations of e.g. the MWF's composition, concentration, supply pressure, or age, the amount of information given in scientific publications should be increased considerably. The poor comparability and reproducibility resulting from the lack of given information is one of the biggest difficulties for researchers working on cross-interdisciplinary progress regarding MWF-application. The more relevant a paper is for MWF-research, the more information must be provided.

The detailed composition of MWFs often is not known by the user due to the understandable interest of MWF-producers to keep their formulations secret. Nevertheless, papers which deal with a variation of MWFs (e.g. regarding the concept, the composition, or the supply-strategy) should provide as much information as possible in a comprehensible way. Thus, standardized parameter-presentation at least for CIRP papers is proposed. Fig. 34 presents an example for a compressed way to summarize the most relevant parameters regarding MWF-composition and supply.

For two generally different ways of MWF-application in manufacturing processes (oil-based MWF, water-based MWF), the most important parameters are exemplarily given. Besides the general MWF-concept and the type of MWF chosen for the experiments, also the base fluid should be indicated to allow for assessment e.g. of environmental impacts. MWF-producers compose the products in a way to meet the requirements of specific tribological systems. Therefore, they usually recommend their

MWF-Concept	Dry	MQL	Flood	Cryo	Solid		
MWF-Type	X	Oil	Emulsion	Solution			
Base Fluid Ressource	X	Mineral	Veget.	Animal	Ionic	Other	
Recommended Workpiece Material	X	SC	SS	NI	CE	FR	M
Recommended Process	X	C	G	F	E	M	
MWF-Age [years]	X	New	< 1	> 1			
Conc. concentrate [%]	0	5	10	15	20	25	Other
Q_MWF [l/min ; g/min]	0	1	10	100	1000	Other	
v_jet [m/s]	0	1	10	100	1000	Other	
			40	25			

Fig. 34. Proposed approach for a condensed way of summarizing MWF-relevant information in future CIRP publications.

MWFs for the processing of one or more workpiece materials. In Fig. 34, SC stands for non-stainless (carbon-) steel, whereas stainless steels (SS), non-iron metals (NI), ceramics (CE), and fiber-reinforced materials (FR) are covered by other abbreviations. For all parameters in Fig. 34, multipurpose is indicated by choosing the M whereas an X indicates that this category is not applicable (e.g. MWF-age in dry machining) or a parameter is simply not known. The abbreviations regarding the process a MWF is recommended for by the MWF-producer are oriented towards the CIRP scientific technical committees (C = cutting, G = abrasive processes, F = forming, E = EDM/ECM, M = multipurpose). The elapsed service life (MWF-age), its concentration, as well as the flow rate Q and the MWF-jet velocity v_{jet} are further parameters which should be provided mandatorily in publications dealing with MWFs. If available, additional information (e.g. on the concentration of specific additives) however is always helpful. Thus, it would be possible to add the explicit value of the parameter (e.g. $v_{jet} = 40 \text{ m/s}$ for the oil-based MWF in Fig. 34).

These specifications are no substitute for the process parameters of a manufacturing process but additional information to be disclosed within scientific publications. The findings summarized in this paper indicate that MWFs may be as important for the result of manufacturing processes as parameters like feed, cutting/forming speeds, depth of cut, etc. A consistent incorporation of additional MWF-related information into CIRP papers would be useful given the significance of MWFs in manufacturing processes.

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