Chapter 33

Metalworking Fluids

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33.1 Metalworking Fluids: Usage and Ingredients

Metalworking fluids (MWF) are used in metal processing for cooling and lubricating purposes, for corrosion inhibition, and for flushing away of metal chips. Two groups of MWF can be distinguished: water-based MWF (wb MWF), usually emulsions, which are prepared at the metalworking company by aqueous dilution of a concentrate delivered by the lubricant producer, and neat oils, which are non-water-miscible oily preparations used as obtained from the manufacturer. Wb MWF are used in the drilling, cutting, turning, and grinding of metal parts, neat oils in cutting, grinding, and honing. Their complex composition is commonly based on mineral oils or (semi-) synthetic hydrocarbon compounds. Various admixtures, such as emulsifiers, buffers, stabilizers, anti-fog-additives, foam inhibitors, tensides, solubility enhancers, lubricants, corrosion inhibitors, extreme-pressure-additives, and biocides (bactericides and fungicides), are usually added, according to the respective needs [3, 5, 6, 20, 30, 70, 72]. In the comments on the German occupational exposure threshold limit values (MAK-Werte) published in 2000, more than 200 components used in MWF are listed [6]. During the working process, wb MWF are subject to change: the concentration may rise due to the vaporization of water, the emulsion might break, and the pH may shift due to heating at the workpiece or due to bacterial contamination. Biocides other than those contained in the original MWF may be added to prevent microbial growth during the long time of use, and slideway oils or hydraulic oils from the processing machines may be introduced into the MWF by leakage [26, 30, 70, 72].

Core Message

- Two types of metalworking fluids (MWF) can be distinguished: water-based MWF (wb MWF) and neat oils. Their composition is complex. Many components and additives are in use. Wb MWF are subject to change during the working process.

33.2 Occupational Skin Disease due to Metalworking Fluids

Occupational contact dermatitis (OCD) is common in metalworkers exposed to MWF [2, 9, 14, 15, 22, 34, 35, 61, 62]. In an epidemiological study on 286 metalworkers exposed to MWF, de Boer et al. found hand dermatitis in 26% of the employees [14, 15]. Of 201 trainees, 47 (23%) had had hand dermatitis at least

once during the study period of 2.5 years in the Swiss Prospective Metal Worker Eczema Study (PROMETES) [9]. The 3-year-incidence of hand eczema was 15.3% among metalworker apprentices in a German prospective cohort study in the car industry (PACO-study) [22]. Recently, in a Swedish cross-sectional study on 163 MWF-exposed metalworkers with skin complaints, OCD was diagnosed in 14.1% [35]. In these and other studies on OCD in metalworkers [2, 34], irritant contact dermatitis (ICD) was more frequently observed than allergic contact dermatitis (ACD). However, as in any other comparable occupational situation, irritant contact dermatitis promotes, and often precedes, sensitization [39]. Hence, the frequency of ACD in a given study population depends on the average duration of exposure and skin disease. Moreover, a simple dichotomization in ICD and ACD does not reflect reality, since other factors such as atopy are also important, and in most cases, the occupational skin disease is a mixture of constitutional and irritant and/or allergic contact dermatitis [5, 30, 34, 61, 62, 69]. It is likely that contact allergy due to MWF is under-diagnosed because not every possible allergenic substance is being tested in the patients concerned [26, 66].

Clinically, OCD due to MWF usually presents as vesicular or rhagadiform eczema of the web spaces, the lateral aspects of the fingers, and the backs of the hands. Often, the dermatitis spreads to the palms and the wrists up to the forearms. Bacterial superinfections are possible [2, 20, 61, 62]. MWF dermatitis may have an unsatisfactory prognosis. Pryce et al. performed a follow-up study on 121 metalworkers concerned, and found skin symptoms in more than 70% of the patients still present after two years, partly in spite of job discontinuation [61]. Shah et al. made similar findings [68]. However, the authors admit that the outcome depends very much on the individuals concerned, particularly on the patients' understanding of the cause of the disease and on their willingness to change their behavior at the workplace.

Core Message

- MWF are a frequent cause of occupational contact dermatitis (OCD), with irritant contact dermatitis (ICD) being diagnosed more often than allergic contact dermatitis (ACD). However, in most cases, the occupational skin disease is a mixture of constitutional dermatitis, ICD, and/or ACD. Contact allergy due to MWF may be under-diagnosed.

33.3 Irritant Contact Dermatitis due to Metalworking Fluids

MWF, in particular wb MWF, exhibit irritant effects to the skin. Due to the risk of injury from rotating tools, it is prohibited to wear protective gloves at most MWF workplaces (Fig. 1). Skin irritation by wb MWF is not only caused by wet work, but also by the alkaline pH, usually ranging from 8.5 to 9.6 [72]. Additionally, emulsifiers damage the epidermal barrier and biocides have irritant properties [61, 62]. In many workplaces, there is no continuous exposure to wb MWF, but the skin is contaminated at some repetitive operations, e.g., when changing the workpiece. Mostly, the wb MWF splashes are not removed for other operations, such as control measurements or burr removing. They dry up on the skin within few minutes, and, as a consequence, the wb MWF is concentrated due to vaporization, and irritancy increases [48]. Additionally, it could be shown in the PROMETES study that not only chemical irritation, but also mechanical factors play a role in the damage of the epidermal barrier in metalworkers [9]. Moreover, in metal processing, as in any other comparable occupational setting, a too short recovery time after repetitive minor irritant exposures eventually leads to clinically visible irritant skin damage, following the model described by Malten [9, 52].

Core Message

- In most MWF workplaces, no gloves are allowed. Irritant effects of wb MWF are due to wet work, alkalinity, emulsifiers, and biocides. In wb MWF splashes that dry up on the skin, concentration of the components increases within minutes, thus, enhancing irritancy.

33.4 Contact Allergy due to Metalworking Fluids

In 1985, Alomar et al. found an increased number of contact allergies to *para*-phenylenediamine (PPD), dichromate, and cobalt in the standard series, and to benzisothiazolinone (BIT), 1,3,5-tris(2-hydroxyethyl)-hexahydrotriazine (Grotan BK), and triethanolamine (TEA) in a MWF test series in their study on 230 MWF-exposed metalworkers with OCD [2]. However, the clinical relevance of the positive reactions to the standard series allergens could not be stated def-

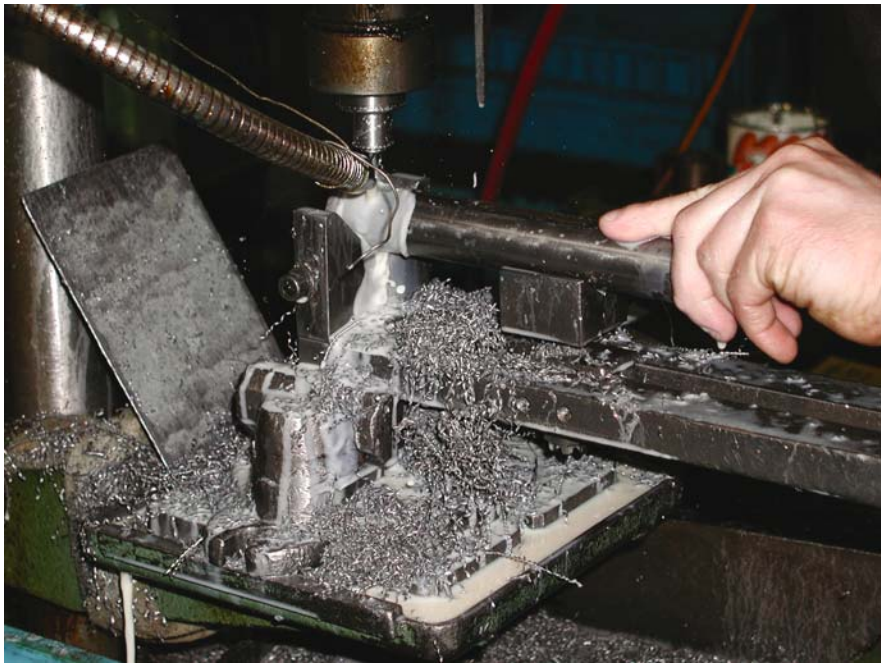

Fig. 1.
Drilling with wb MWF. The worker's hand is permanently wetted with MWF. No gloves are allowed at this workplace because of the risk of injury from rotating tools (courtesy of Dr. H.-G. Englitz)

initely in most cases [2]. In a study performed in 1986/1987 on 174 patients with suspected MWF dermatitis, Grattan et al. saw an increase of sensitizations to nickel, colophonium, formaldehyde, the formaldehyde releaser Dowicil 200 (Quaternium 15), and other biocides [34]. In 1989, de Boer et al. published an investigation on 286 metalworkers exposed to MWF, of which, 75 had had hand eczema. A patch test was performed in 40 of these 75 patients, and 8 of them had a contact allergy [15]. Occupational sensitizations in these cases were due to formaldehyde and 5-chloro-2-methylisothiazol-3-one/2-methylisothiazol-3-one (MCI/MI) [15]. Nethercott et al. investigated 27 metalworkers exposed to MWF with hand dermatitis in 1990. Thirteen of these patients had had ACD, and 11 of them were sensitized to MCI/MI, which was used in the MWF [57]. At the beginning of the 1990s, two retrospective studies on contact allergies in metalworkers were published by the Information Network of Departments of Dermatology (IVDK). However, these data analyses were focused neither on patients exposed to MWF nor on those with OCD. In both analyses, a surprisingly high frequency of sensitizations to p-aminoazobenzene (PAAB) was found [73, 74]. Brinkmeier et al. performed an investigation on 408 metalworkers and found positive patch test reactions to Biobans P 1487, CS 1246, and CS 1135 in 13 patients (3.4%). Most of the test reactions were weak positive and could be reproduced on re-testing in only 2 out of 10 patients [11]. In the course of a large German study on contact allergies among patients with OCD (FaSt study), 160 metalworkers were investigated from 1999 to 2001 [32]. Most frequently, sensitizations to monoethanolamine (MEA), colophonium/abietic acid, and fragrance mix were observed. Additionally, cobalt, diethanolamine (DEA), formaldehyde, formaldehyde releasers, and other biocides were important allergens in these patients. Metalworkers exposed to wb MWF with OCD had a significantly increased risk of sensitization to colophonium, formaldehyde, and fragrance mix when compared to metalworkers with OCD who were *not* exposed to wb MWF, or men not working in the metal industry [32]. Recently (2003), a Swedish study on OCD among the employees of a metalworking plant was published by Gruvberger et al. [35]. Of 164 metalworkers with skin complaints, 10 were found to have occupationally induced ACD, and 4 of them were sensitized to BIT, while 3 patients had a contact allergy due to the extreme-pressure-additive ethylhexylzinc dithiophosphate (EHZDTP) [35].

During the last decade, sensitizations to the following MWF components have been reported in case reports of metalworkers with OCD: diglycolamine [28], ethylenediamine [13], also possibly as indicator for a sensitization to other amines [19], MEA [47, 58], alkanolamineborates [12], a condensate of boric acid, MEA, and fatty acids [43], fatty acid polydiethanolamide [45], oleyl alcohol [47], tertiary-butylhydroquinone [54], imazalil [60], iodopropynyl butylcarbamate [51], sodium pyrithione [41, 49], ethylhexylzinc dithiophosphate [42, 45], and oak moss resin [58].

Core Message

- In several studies, formaldehyde and other biocides, particularly formaldehyde releasers, were frequent MWF allergens. Additionally, sensitizations to colophonium/abietic acid, *para*-phenylenediamine (PPD), *para*-aminoazobenzene (PAAB), dichromate, and cobalt have been described, but the clinical relevance of these findings could not always be established. In case reports, a variety of other allergens in MWF have been described.

33.5 Important Allergens in Metalworking Fluids

33.5.1 Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), and Diglycolamine

In wb MWF, MEA, DEA, and TEA are used as rust preventive agents with emulsifying properties, while diglycolamine serves as emulsifier. MEA ranked first among the allergens in wb MWF in two recent studies [31, 32]. MEA may be present in the MWF as reaction products of MEA with boric acid or other MWF components, and probably only a certain fraction of MEA is present as such. Cases of contact allergy due to such reaction products have been reported, partly without reaction to MEA [12, 43]. Due to a potential formation of carcinogenic N-nitrosamines, the concentration of DEA is limited to 0.2% in the MWF concentrate in Germany by law since 1993 [4]. Due to this limitation, the use of DEA in wb MWF has declined in the following years. This is probably reflected by the far lower frequency of sensitizations to DEA compared to MEA in the two above-mentioned recent German studies [31, 32]. TEA, which is also frequently used as an emulsifier in creams and cosmetics, was found to be a rare MWF allergen. However, we have no information on the extent of its use in MWF currently on the market. Thus, the very low proportion of patients allergic to TEA may be either due to a lower sensitizing capacity, which could be explained by a lower reactivity due to its chemical structure, or due to a less frequent use in wb MWF. Diglycolamine was first described as an MWF allergen in 2002 [28], and was not included in a MWF test series before 2003 [31]. Hence, experience with this substance is still limited, but it seems to be an important MWF allergen though.

33.5.2 Colophonium/Abietic Acid

A positive patch test reaction to colophonium indicates a sensitization to oxidation products of abietic acid and other resin acids which are contained in colophonium [38]. The concentrate of a wb MWF may contain 4–8% (in some cases, up to 10%) distilled tall oil (DTO). Usually, this concentrate is diluted with water down to 5%. In this case, the concentration of DTO in the final wb MWF (to which the metalworker is exposed) is in the range 0.2–0.4%. According to information from the industry, about 30% of the DTO are resin acids, and of these, about one third is abietic acid. In other words: the content of resin acids in the wb MWF is 0.06–0.12%, the content of abietic acid is 0.02–0.04%. On exposure to air, which occurs during normal use of wb MWF, the resin acids oxidize rather quickly [36, 37, 46]. The fact that resin acids form alkanolamine salts in the wb MWF probably has no influence on the oxidation because different parts of the resin acid molecules are involved in the formation of salts and the oxidation process, respectively [37]. The concentration of resin acids in the wb MWF may seem rather low. However, in most workplaces, the wb MWF dries up on the contaminated skin, and the concentration rises within minutes [48]. If, furthermore, the irritant damage to the epidermal barrier of the exposed skin is taken into account, occupational exposure to wb MWF carries a high risk of sensitization. This is illustrated by epidemiological data. In the above-mentioned FaSt study (1999 to 2001), metalworkers with OCD and exposure to wb MWF had an eightfold increased risk of sensitization to colophonium [odds ratio (OR) 8.0; 95% confidence interval (CI) 1.7–73.5] when compared to metalworkers with OCD who were *not* exposed to wb MWF [32].

33.5.3 Fragrances

In the same study, metalworkers exposed to wb MWF with OCD had an increased risk of sensitization to fragrances in terms of positive patch test reactions to fragrance mix and to *Myroxylon pereirae* (MPR; balsam of Peru) when compared to metalworkers with OCD who were *not* exposed to wb MWF [32]. If the use of barrier creams or emollients was taken into account in an adjusted logistic regression analysis, the

risk estimate was somewhat even higher. This strongly indicated that the exposure to wb MWF itself was the relevant risk factor. Until about 1990, fragrances or odor masks, even MPR, were mentioned as common components of wb MWF [15, 40, 62]. According to recent information from the lubricant producing industry, normally, no fragrances are added to the MWF concentrate nowadays. However, it cannot be excluded that odor masks are added by the metalworking companies during the usage of the wb MWF. Corresponding products are being offered on the market. Of course, this does not imply that every fragrance allergy in exposed metalworkers is acquired by wb MWF. In every individual case, a complete history has to be taken carefully, particularly with respect to other allergen sources (aftershave, deodorant etc.). Sometimes, however, this investigation will reveal occupational causation of fragrance allergy induced by wb MWF [58].

33.5.4 Cobalt, Nickel, Dichromate

Six comprehensive studies on cobalt, nickel, and dichromate in MWF have been published so far [16, 17, 50, 55, 59, 79]. In most of these studies, analyses were performed by atomic absorption spectrometry (AAS), and mostly, it was not stated whether the contents of metal particles (abrasion of tools or workpieces) or of metal ions was determined. The valence state of the metal ions was not investigated. The "bioavailability" was not fully elucidated; hence, it cannot be excluded that, in some cases, hardly soluble metal oxides or metal sulfides were described, which are not as important from the allergological point of view. The results of these studies can be summarized as follows: cobalt, nickel, and chromium are not present in fresh, unused MWF (concentration <1 ppm). The presence of cobalt in used MWF mainly depends on the metals or alloys processed. If no cobalt-containing hard metals were processed, the cobalt concentration was usually below 3 ppm. When processing hard metals containing cobalt, the cobalt concentration was up to 300 ppm, in single cases, even up to 550 ppm. The elicitation threshold in patients allergic to cobalt is regarded to be about 100 ppm to 1,000 ppm cobalt ions [65, 78]. In predamaged skin, reactions could even be elicited with 10 ppm cobalt [1]. Hence, if cobalt is present as dissolved ions, concentrations found in MWF which are used in hard metal processing could be sufficient to elicit an allergic reaction, possibly even to induce sensitization. In the above-mentioned studies, concentrations of nickel and chromium in used MWF were usually below 1 ppm. However, there were some exceptions, with concentrations of nickel up to 130 ppm and of chromium up to 280 ppm, which might be sufficient for elicitation in high-grade sensitized individuals, provided the metals are present in a suitable, ionized form. If chromium is present in the hexavalent state, an induction of contact allergy seems possible with the exceptionally high concentrations mentioned, whereas the induction of nickel allergy seems unlikely this way.

In two studies, an increased frequency of cobalt allergies among metalworkers with OCD exposed to MWF was found [2, 32], and in one study each, an increase of sensitizations to nickel [34] and dichromate [2], respectively, was described. However, the clinical relevance of these findings could not be clearly established. In a multifactorial analysis of data from the IVDK in more than 80,000 patients, Uter et al. could not find an increased risk of sensitization to cobalt, nickel, or dichromate in metalworkers [76]. Hence, in each case of contact allergy to these metals in metalworkers exposed to MWF, it is mandatory to elucidate the source of exposure and to establish clinical relevance of the positive test reaction. Occupational exposure other than MWF (e.g., workpieces, tools, handles) or private exposure (e.g., jeans button, costume jewelry, piercing) has to be considered.

33.5.5 Formaldehyde and Formaldehyde Releasers

Several years ago, it was common to use formaldehyde solution for additional preservation of wb MWF during usage, but this seems to be obsolete today. Nowadays, usually formaldehyde releasers, mainly *O*-formals (acetals, semiacetals) and *N*-formals (aminals, semiaminals) are used for the preservation of wb MWF and in system cleansers [26, 71]. The amount of formaldehyde released varies, depending on various factors such as pH, temperature, microbial contamination, etc. [25]. Peak formaldehyde concentrations may arise from additional preservation during the usage. An increased frequency of sensitizations to formaldehyde among metalworkers with OCD exposed to wb MWF has been known from studies in the 1980s [15, 34]. In the FaSt study (1999 to 2001), it could be shown that the risk of formaldehyde allergy was significantly increased in these patients when compared to men not working in the metal industry (OR 4.1; 95% CI 1.5–9.2) [32]. In the above-mentioned multifactorial IVDK data analysis of 80,000 patients, the metalworkers' risk of formaldehyde allergy ranked second after health care workers, who are exposed to it by disinfectants [76]. Sensitizations to formaldehyde releasers may be directed

against the whole molecule or the formaldehyde released. There is only a limited correlation between the ability to release formaldehyde and concomitant patch test reactions to formaldehyde and the releaser [25]. Studies on this subject are hampered by the fact that patch test reactions to formaldehyde releasers are often weak and poorly reproducible [11, 25].

33.5.6 Methyldibromo Glutaronitrile (MDBGN) and 2-phenoxyethanol (PE)

Methyldibromo glutaronitrile (MDBGN) has been used some years ago for the preservation of wb MWF. According to information from the lubricant industry, it is currently not in use for this purpose [26]. However, the occurrence of MDBGN as a preservative in creams, cosmetics, and skin care products dramatically increased in the 1990s, and the frequency of corresponding sensitizations rose in parallel [24, 80]. Hence, metalworkers may have acquired sensitization to MDBGN by protective creams or emollients, or by private skin care products as well as by wb MWF formerly. In the standard series, MDBGN is routinely tested in combination with PE at a total concentration of 1% because this mixture has frequently been used as a preservative. However, PE, which, in contrast to MDBGN, is still in use as a preservative in wb MWF, plays no role as a sensitizer. So, in the vast majority of the cases, MDBGN is the relevant allergen in positive test reactions to MDBGN/PE [24, 27]. In the MDBGN/PE combination used, MDBGN has a test concentration of 0.2%. Patch testing with MDBGN 0.3% leads to more positive reactions, of which, according to a study of the German Contact Dermatitis Research Group (DKG), many are probably irritant, i.e., false-positive [27]. Hence, particularly when testing with MDBGN in high concentrations, the clinical relevance of every positive reaction has to be established, taking into account both domestic and occupational exposure, including skin care at work.

33.5.7 5-Chloro-2-methylisothiazol-3-one/ 2-methylisothiazol-3-one (MCI/MI)

Due to its chemical properties, MCI/MI is not used as a preservative in the MWF concentrate, but it may be added to the wb MWF at the workplace as an additional biocide (top up biocide) [26]. Particularly in the beginning of the 1990s, MCI/MI was very frequently found as a preservative in skin care products, but in the following years, its use declined dramatically due to the "epidemic" of sensitization in these years [56]. Recently, MCI/MI has come back into this field, albeit with lower concentrations, which will probably not induce new sensitizations [18, 63]. Hence, the particular exposure to MCI/MI has to be established in every metalworker sensitized with special regard to additional preservation of the wb MWF during its use. Benzisothiazolinone (BIT) and octylisothiazolinone (OIT), which are also currently used for the preservation of wb MWF, do not cross react with MCI/MI [23].

33.5.8 Other Biocides

As mentioned above, various other biocides, particularly formaldehyde releasers and other isothiazolinones, such as BIT and OIT, are being, or have been, used as preservatives in wb MWF, and cases of sensitization have been observed. Corresponding test substances are part of the respective MWF test series (see below). Iodopropynyl butylcarbamate (IPBC) had been tested at 0.1% pet., which was too low a test concentration. Hence, sensitizations remained undetected [67]. As the result of a corresponding study, the DKG recommends to test IPBC at 0.2% pet. [10]. In every case of a metalworker with OCD, a detailed history including additional preservation of the MWF during its use has to be taken and, in case of a weak or doubtful patch test reaction to biocides, a repeated open application test (ROAT) or provocative use test (PUT) can be recommended.

33.5.9 *p*-Aminoazobenzene (PAAB)

p-Aminoazobenzene (PAAB) is tested as a marker for contact allergy to para di-substituted aromatic amines or azo dyes [77], and was part of the MWF patch test series. Until the beginning of the 1990s, it was common to dye MWF [40, 62] partly with azo dyes. Nowadays, MWF are produced without dye, but occasionally, some metalworking companies add colors to their MWF systems. In contrast, most technical oils, such as hydraulic oils or slideway oils, are colored, but azo dyes should not be used for this purpose [30]. MWF often become contaminated with these technical oils by leakage and, thus, they might be a source of exposure to dyes for the metalworker. However, while concomitant reactions to PAAB and PPD are frequent and probably indicate a contact allergy to para-amino compounds [77], we know from the analysis of data concerning allergic reactions to textile dyes that PAAB is not a reliable marker for

contact allergy to azo dyes [8]. An increased risk of active sensitization has been described when PAAB and PPD are patch tested in parallel [7]. In view of these circumstances, PAAB should be deleted from the MWF test series, although it was one of the frequent allergens in a recent IVDK data analysis [31]. In the cases concerned, which may, however, not easily be suspected, the actual dyes in technical oils from the patients' workplace should be tested instead.

33.6 MWF Patch Test Series

Patch test series for diagnostics in metalworkers are commercially available. However, regarding the wide variety of substances and components used in MWF [6], it seems likely that relevant contact allergies may be overlooked because far from all potentially allergenic MWF components are available as standardized patch test preparations. Additionally, the composition of MWF changes with time, due to technological progress. Hence, for a valid allergy diagnostic in this field, it is important to continuously adapt the MWF test series to the current spectrum of occupational exposure. In 2000, the interdisciplinary working party on allergy diagnostics in the metal branch compiled two lists of MWF allergens commercially available as patch test substances [26]. The first list contains substances currently used in MWF, and the second list contains substances that have only been used previously, mostly before 1994 [26]. Based on this information, at the end of 2001, the DKG established two corresponding MWF series. These series are to be tested in patients with suspected ACD and exposure to MWF in addition to the standard series, the ointment base series, and the preservative series. This design was chosen because it usually makes sense also to test the latter two series, as skin care products are another possible allergen source in metalworkers with suspected OCD. To avoid duplicate patch tests, the DKG omitted from the MWF series those potential MWF allergens that are contained in the standard, ointment base, or preservative series. Recently, results with these test series have been evaluated [31]. Based on this data, current and former MWF allergens which should be tested in metalworkers with suspected MWF dermatitis are compiled in Tables 1 and 2.

The allergological diagnostic in MWF dermatitis has improved a great deal during the last years. Principally, there are two possible ways to maintain its diagnostic value. First, frequently used MWF components that are not investigated sufficiently regarding their allergenic potential can be tested systematically in clinical studies. In a study of that kind, diglycolamine has been found to be a relevant MWF allergen recently [29]. Second, MWF from the patient's workplace and their components should be tested in every case concerned.

33.7 Patch Testing with MWF from the Patient's Workplace

Patch testing with MWF from the patient's workplace is an important additional diagnostic tool in patients with suspected MWF dermatitis, which has been employed in several studies on occupational dermatitis in metalworkers [2, 15, 34, 35]. However, in these studies, as in published recommendations for patch testing with MWF, test concentrations and vehicles have varied greatly [2, 15, 20, 21, 34, 35, 44]. A recent retrospective study on MWF patch tests in 141 metalworkers showed that MWF can be tested at workplace concentration and neat oils at 50% in olive oil without undue risk of irritant test reactions [33]. With lower concentrations, relevant allergic reactions might be missed.

The interdisciplinary working party on allergy diagnostics in the metal branch has published recommendations on how to patch test MWF from the patient's workplace in 2002 [72]. The essential points of these recommendations, which are as yet published in German only, are: of every MWF used by the patient, two samples should be taken, i.e., one fresh and one used sample. In the case of wb MWF, a sample of the fresh, undiluted MWF concentrate should be obtained. The used samples are to be taken from the inflows of the machines (and not from the so-called sumps) to avoid contamination with metal chips, which might cause irritant patch test reactions. Samples of used wb MWF must be stored in a refrigerator, and be tested within 3–5 days, as otherwise, microbial contamination will change or even destroy the emulsion. Fresh concentrate of the wb MWF should be tested 5% aq., which is an average workplace concentration. Used wb MWF can be patch tested as is, provided that the concentration at the workplace is ≤8%. In the case of higher workplace concentrations, further dilution to an end concentration of 4–8%, as required, is recommended. As a rule of thumb, this can be achieved by a 1:1 aqueous dilution of the wb MWF. Usually, wb MWF are alkaline (pH 8.6–9.5), but experience shows that this is tolerated by patients on patch testing. Neat oils should be tested 50% in olive oil. Used wb MWF samples must be accompanied by information about the concentration and pH at the time of sampling, date of the last change of the MWF, system cleaner used, date of last preservation, name of bactericide and fungicide

Table 1. Current MWF allergens to be tested in metalworkers with suspected MWF dermatitis (modified from [26, 30, 31])

No.	Substance	Occurrence in MWF	Function in MWF	Patch test concentration
MWF series (current allergens)				
1	Benzylhemiformal	wb MWF	Biocide, formaldehyde releaser	1% pet.
2	4,4-Dimethyl-1,3-oxazolidine/3,4,4-trimethyl-1,3-oxazolidine (Bioban CS 1135)	wb MWF	Biocide, formaldehyde releaser	1% pet.
3	7-Ethylbicyclooxazolidine (Bioban CS 1246)	wb MWF	Biocide, formaldehyde releaser	1% pet.
4	Iodopropynyl butylcarbamate (IPBC)	wb MWF	Biocide	0.2% pet.
5	*N,N′*-Methylene-bis-5-methyl-oxazolidine	wb MWF	Biocide, formaldehyde releaser	1% pet.
6	1,2-Benzisothiazolin-3-one, sodium salt	wb MWF	Biocide	0.1% pet.
7	Octylisothiazolinone	wb MWF	Biocide	0.025% pet.
8	2-Phenoxyethanol	wb MWF	Biocide	1% pet.
9	Sodium-2-pyridinethiol-1-oxide (sodium omadine)	wb MWF	Biocide	0.1% aq.
10	1,3,5-Tris(2-hydroxyethyl)-hexahydrotriazine (Grotan BK®)	wb MWF	Biocide, formaldehyde releaser	1% pet.
11	Benzotriazole	wb MWF and neat oils	Rust preventive	1% pet.
12	Diethanolamine (DEA)[a]	wb MWF	Rust preventive	2% pet.
13	Monoethanolamine (MEA)	wb MWF	Rust preventive	2% pet.
14	*p*-tert-Butylphenol	neat oils	Antioxidant	1% pet.
15	Abietic acid	wb MWF	Emulsifier/surfactant	10% pet.
16	Diglycolamine [2-(2-aminoethoxy)ethanol]	wb MWF	Emulsifier	1% pet.
Standard series				
17	Formaldehyde[b]	wb MWF	Top up biocide	1% aq.
18	5-Chloro-2-methylisothiazol-3-one/2-methylisothiazol-3-one (MCI/MI)	wb MWF	Top up biocide	0.01% aq.
19	Lanolin alcohol	wb MWF	Anti-wear additive	30% pet.
20	Zinc diethyldithiocarbamate (ZDEC)[c]	neat oils	Anti-wear additive	1% pet.
21	Cetearyl alcohol	wb MWF	Stabilizer/anti-wear additive	20% pet.
22	Colophonium[d]	wb MWF	Emulsifier/surfactant	20% pet.
23	Mercaptobenzothiazole	wb MWF	Rust preventive	2% pet.
Ointment base series				
24	Propylene glycol	wb MWF	Stabilizer	5% pet.
25	Polyethylene glycol (tested as polyethylene glycol ointment base)	–	Stabilizer/anti-wear additive	100%
26	Triethanolamine (TEA)	wb MWF	Rust preventive	2.5% pet.
27	Butylhydroxy toluol (BHT)	Neat oils	Antioxidant	2% pet.
Preservative series				
28	Triclosan	Neat oils	Biocide	2% pet.

[a] Use in MWF limited by law in Germany since 1993
[b] Released from formaldehyde releasers
[c] Tested as a marker for sodium diethyldithiocarbamate
[d] Allergic reaction indicates contact allergy to oxidation products of resin acids

Table 2. Former MWF allergens to be tested in metalworkers with suspected MWF dermatitis (modified from [26, 30, 31])

No.	Substance	Occurrence in MWF	Function in MWF	Patch test concentration
MWF series (former allergens)				
1	Chlorocresol	Neat oils	Biocide	1% pet.
2	Chloroxylenol	wb MWF	Biocide	1% pet.
3	Dipentene (d,l-limonene)	wb MWF	Biocide	2% pet.
4	Hexamethylene tetramine	wb MWF	Biocide	1% pet.
5	2-Hydroxymethyl-2-nitro-1,3-propanediol (Tris Nitro)[a].	wb MWF	Biocide, formaldehyde releaser	1% pet
6	Methyldibromo glutaronitrile (MDBGN)	wb MWF	Biocide	0.3% pet.
7	4-(2-Nitrobutyl) morpholine/4,4´-(2-ethyl-2-nitro-trimethylene) dimorpholine (Bioban P 1487)[a]	wb MWF	Biocide, formaldehyde releaser	1% pet.
8	Morpholinyl mercaptobenzothiazole (MOR)	wb MWF	Rust preventive	0.5% pet.
9	Ethylenediamine dihydrochloride	wb MWF	?	1% pet.
Standard series				
10	Paraben mix	wb MWF	Biocide	16% pet.
11	Methyldibromo glutaronitrile/2-phenoxyethanol (MDBGN/PE)[b]	wb MWF	MDBGN: biocide	1% pet.
12	*Myroxylon pereirae* resin (MPR, balsam of Peru)	wb MWF	Odor mask	25% pet.
13	Fragrance mix[c]	wb MWF	Odor mask	8% pet.
Ointment base series				
14	Coconut diethanolamide[a]	wb MWF	Emulsifier	0.5% pet.
Preservative series				
15	Bronopol (2-bromo-2-nitropropane-1,3-diol)[d]	wb MWF	Biocide, formaldehyde releaser	0.5% pet.
16	Chloroacetamide	wb MWF	Biocide	0.2% pet.

[a] Prohibited in MWF by law in Germany since 1993
[b] In contrast to PE, MDBGN is probably no longer used in MWF
[c] It is unclear which fragrances are used in MWF, if at all
[d] No longer used in MWF, but is used in skin care products

used, name of other additives and date of addition, material processed in the machine, and possible influx of hydraulic oils, slideway oils, or other oils by leakage. For neat oils, only data on the last change of the MWF, additives, material processed in the machine, and possible influx of other oils needs to be documented. Drafts of information sheets and test protocols, as well as instructions for patch testing can be downloaded in the German language at http://www.ivdk.org (section on "downloads") or at http://www.hautstadt.de as part of a training course for patch testing with material brought in by the patient.

The interdisciplinary working party emphasizes that false-negative test reactions to MWF may occur, even under the recommended conditions [72]. Allergenic components in the MWF may be diluted too much, and, thus, may elicit no reaction on patch testing in the intact skin of the upper back, although they may cause ACD on the pre-damaged skin of the hands under workplace conditions. Hence, patch testing with the single components of the MWF should not only be performed in case of a positive patch test reaction to the MWF from the workplace, but also in clinically suspected cases, in whom no test reaction to the individual MWF could be seen [53, 64]. However, to obtain maximum benefit from a breakdown test with single components of the MWF, complete information on the ingredients and additives of the MWF must be at hand. To obtain detailed, allergologically useful information about the ingredients and additives of an MWF is a very time-consuming business. First, the patient and his/her employer have to cooperate in providing information about the workplace exposure, in particular, correct identification of the products and batches used and their manufacturers. In the material safety data

sheets of the MWF, far from every component that might be responsible for the individual patient's disease is listed. Usually, only those chemicals are named which are known sensitizers, and are present above a threshold concentration which requires labeling with the risk phrase R 43. If mentioned at all, chemicals may be denoted using synonyms not known to the clinician. Some lubricant producers are very co-operative and readily supply additional information, while others are not. As time is limited in the hospital routine, these difficulties are presumably one reason why additional diagnostics are rarely performed, and why the clinical relevance of positive reactions to standardized MWF allergens often remains unclear in the individual case. The adequate concentration for patch testing of many MWF components does not necessarily correspond to their use concentration in the MWF. Thus, performing a breakdown test with the single MWF components is hampered by uncertainty concerning correct patch test concentrations (on the producer's as well as on the physician's part), and, consequently, uncertainty about interpreting test reactions with these preparations. Additionally, often, the producers cannot deliver chemically defined components, since reaction products may be formed in the production process of the MWF which are not completely characterized. In this connection, reaction products of boric acid and alkanolamines may serve as an example: usually, more than one alkanolamine, such as MEA, diglycolamine etc., is added to the MWF base, which contains boric acid, and the reaction products are not analyzed. Hence, contact allergy to these reaction products – although well known from several case reports [12, 43] – is not easy to diagnose.

Against this background, we propose a center for information and documentation of contact allergies due to occupational exposure (German acronym: IDKB, from "Informations- und Dokumentationsstelle für Kontaktallergien durch Berufsstoffe"), which should work like the "IDOK," which successfully does the same work in the field of cosmetics and skin care products [75], and could provide:

- Support in obtaining information on, and samples of, single constituents of the occupational material (workplace MWF)
- Help in finding adequate patch test preparations
- Central documentation of patch test results and detection of new allergens
- Quality control of patch testing by continuous adaptation of test recommendations

Core Message

- Patch testing with MWF from the patients' workplace is a time consuming, but very useful additional diagnostic step which is not easy to perform correctly. Recommendations for the adequate performance are available in German at http://www.ivdk.org (section on "downloads") or at http://www.hautstadt.de as part of a training course for patch testing with material brought in by the patient.

33.8 Preventive Measures

Working with wb MWF is connected with wet work, and corresponding preventive measures have to be taken. Additionally, some peculiarities should be considered. If the skin is wetted with MWF only intermittently, the MWF should not dry up on the skin, but should be removed in order to avoid a rise in concentration by the vaporization of water and the resulting increase of irritancy. Cleaning clothes used for tools or workpieces should easily be distinguishable from those for wiping off the hands. Skin contact with MWF should be minimized by automation, encapsulation of machines, etc. For the degreasing of workpieces, hooks, sieves, or similar devices should be used for immersing, thus, reducing the alternating skin irritation by MWF and solvent.

Pollution of the MWF by dirt, food, etc. has to be avoided. Workplaces have to be kept clean. The concentration and pH of the MWF have to be controlled weekly in order to recognize and eliminate any increase of concentration or pH in time. Bacterial contamination itself does not affect skin irritancy of the MWF. However, there is an indirect effect because, in case of a too high microbial colonization, additional preservation is necessary due to technical reasons. Every additional preservation has to be documented exactly (date, amount, product used). Most suitable, additional preservation is performed after the last shift on Friday, so the biocide is almost completely dispensed at the beginning of work on Monday morning. In companies without a weekend break, as few metalworkers as possible should be exposed to the maximum biocide concentration, and all workers must be informed about the additional preservation. System cleansers should not be used during operation hours as they contain high concentrations of biocides. The same precautions as with additional preservation have to be taken.

At most MWF workplaces, it is prohibited to wear protective gloves because of the risk of injury from rotating tools. If gloves are allowed, a denseness guaranty should be demanded from the glove manufacturer. A skin protection plan has to be set up. For protection against wb MWF, water-in-oil emulsions are recommended. Creams containing tannins may be helpful under gloves. Usually, mild tensides are sufficient for skin cleaning. Regular skin care after work is as important as skin protection before work.

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